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ARTIFICIAL COMPOSITES FOR HIGH TEMPERATURE APPLICATIONS; A REVIEW

M.U. Islam
W. Wallace
A.Y. Kandeil

Division of Mechanical Engineering

Division de génie mécanique

National Research Council Canada

Conseil national de recherches Canada

Canada

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ARTIFICIAL COMPOSITES FOR HIGH TEMPERATURE APPLICATIONS; A REVIEW

COMPOSITES ARTIFICIELS DESTINÉS À DES APPLICATIONS A HAUTE TEMPÉRATURE; UN EXPOSÉ

M.U. Islam
W. Wallace*
A.Y. Kandeil**

* National Aeronautical Establishment
** University of Qatar

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G. McGregor, Head/Chef
Manufacturing Technology Centre
Centre de technologie, fabrication

J. Ploeg
Director/
Directeur

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ABSTRACT

This paper provides a review of developments in artificial, metal and ceramic matrix composites with potential for high temperature applications such as in the hot sections of gas turbine engines. Emphasis is placed on developments which have occured since 1975. An attempt is made to assess the current level of activity and to identify outstanding problems and research directions for the future. To provide a basis for these discussions, the status prior to 1975 is also briefly reviewed.

RÉSUMÉ

Cette communication passe en revue les progrès réalisés dans le domaine des composites à artificielle, métallique et céramique pouvant servir dans des applications comportant des températures élevées, comme dans les turbines à gaz. On s'intéresse surtout aux progrès réalisés depuis 1975. On tente d'évaluer le niveau actuel des activités dans ce domaine, d'identifier les problèmes qui n'ont pas été résolus et de définir l'orientation des recherches futures. De plus, afin de bien situer ces discussions, nous revoyons brièvement la situation d'avant 1975.

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ARTIFICIAL COMPOSITES FOR HIGH TEMPERATURE APPLICATIONS: A REVIEW.

1.0 INTRODUCTION

The demands of the aerospace industry and the need for more efficient ground based heat engines have become the main incentives for the development of new higher performance materials. Most monolithic materials lose strength or degrade in properties at higher temperatures. Superalloys, heat resistant alloys and alloys in general, strengthened by conventional mechanisms such as precipitation hardening or mechanical working, exhibit drastic losses in strength at temperatures over 0.7 - 0.8 of their absolute melting points. Dispersion strengthened materials are stronger and more stable than conventional alloys at higher fractions of their melting points ($\approx$0.9). The use-temperatures of ceramics and glasses are often limited by their softening well below their melting points. In Table - 1 some of the materials suitable for high temperature use are listed along with their melting and probable use temperatures.

It is well known that, by conventional alloying methods, there will not be any significant increase in the use temperature of the superalloys in the future. Refractory metals are not only costly but are in critically short supply, so a wide commercial use is highly unlikely. Ceramics offer potential in demanding environments, however their inherent problem of brittleness has to be tackled.

The reason for the development of new higher temperature materials is not only to increase the temperature capability over the existing materials but also to decrease or eliminate the use of strategic and scarce elements. Table - 2 lists the materials critical to the United States as suggested by the Metals Properties Council in 1983 (1). The United States Bureau of Mines lists chromium, cobalt, manganese and platinum group elements as the four most important, strategic and critical metals (1). Chromium and cobalt are the principal alloying elements in nickel base superalloys, while in cobalt base superalloys, cobalt content can be up to 90 volume percent and the remainder consisting of mostly nickel and chromium. Hence, any successful attempt in reducing the use of these critical elements should be well received.

In the past two decades a new class of materials, known as composite materials, has emerged. Composite materials can be generally defined as materials having two or more inherently different constituents, which may or may not be in chemical equilibrium with each other. On this basis, composite materials can be arbitrarily classified into the following two distinct groups:

a) IN-SITU COMPOSITES
b) ARTIFICIAL COMPOSITES

IN-SITU composites are defined as materials derived from directionally transformed poly-phase materials, particularly directionally solidified eutectics. In these composites the fibrous reinforcing phase is usually in chemical equilibrium with the matrix, as the composition of the melt is adjusted

to produce a eutectic upon directional solidification. Examples of the most promising directionally solidified eutectics include:

$$CoTaC, \quad NiTaC, \quad Ni_3Al - Ni_3Nb \quad \text{and} \quad \gamma \,/\, \gamma' \text{-} \delta$$

The first two eutectics contain about 5-12 volume percent TaC fibres in cobalt or nickel alloy matrices. The latter two eutectic alloys have a lamellar structure consisting of platelets of δ (about 30-40 volume percent) in either γ or $\gamma + \gamma'$ matrix. McLean and Khan (2) have summarized the development and current status of IN-SITU composites with particular emphasis on systems having low concentrations of the critical alloying elements. It was pointed out that composite materials offer promise as substitute materials either for state-of-the-art cast superalloy turbine blade alloys or for similar wrought alloys.

In parallel with the development of IN-SITU or directionally solidified eutectic composites, work has been carried out on artificial composites which are also candidates for use in advanced gas turbine engines. They differ from eutectic composites in that the fibres and matrix phases are not in chemical equilibrium and therefore solid fibres must be blended with the matrix by mechanical means. To facilitate processing, the matrix phase may be either liquid or solid. Artificial composites with lower melting point matrices, such as aluminium, magnesium or titanium are also under development but will not be discussed here. The purpose of this paper is to review developments in artificial composites containing fibres or whiskers in metallic or ceramic matrices for high temperature applications, and to identify outstanding problems and research directions for the future.

2.0 PRE - 1975 STATUS

Several papers published in the mid - 1970's made reference to both eutectic composites and artificial metal matrix composites. A typical example is the paper by Blankenship (3) which reviews the development of disc, blade and vane materials from 1950 to 1975, and which also predicts future use of materials to year 2000 [Figure 1]. Although only twelve years have elapsed from the time of the forecast, the predictions made are withstanding the test of time quite well. Pre - alloyed powder alloys and advanced alloys for discs are now state-of-the-art, oxide dispersion strengthened alloys are receiving increased attention for vane applications and directionally solidified superalloys and eutectics are either in service or are undergoing engine testing. In forecasting developments in blade materials, Blankenship includes as his long term prediction the use of tungsten fibre reinforced superalloy composites for the 1990's and beyond.

A more complete review of the literature published to the end of 1975 reveals a number of other systems [Tables 3-6] which were investigated. Tables 3-6 show that the bulk of the work was indeed performed on tungsten or thoriated tungsten wire contained in various nickel or cobalt alloy matrices. Twenty two out of the thirty two papers identified (4-36) dealt with such systems [Table-3]. However, some other systems were also investigated including various ceramic fibres

(SiC, Si_3N_4, alumina and saphire) embedded in nickel alloy matrices [Table-4], metal fibres (W, Ta, Mo, Ni) embedded in ceramic matrices (Si_3N_4, Al_2O_3, mullite, glass etc.) [Table-5], and ceramic fibres (carbon) in ceramic matrices such as carbon, Al_2O_3, magnesia and various types of glass [Table-6].

Each of these systems, with the exception of ceramic-ceramic composites, has limitations since all contain significant amounts of one or more of the strategic elements, including either tungsten, cobalt, tantalum or niobium. Nevertheless, it might be argued that the ceramic containing systems deserve special consideration since they replace at least part of the usual metal system by up to 75 volume percent using a relatively abundent and inexpensive ceramic component. In the case of ceramic-ceramic systems, there is potentially no need for using any of the scarse strategic elements.

Artificial composites are now commonly referred to as either ductile-ductile, ductile-brittle, brittle-ductile or brittle-brittle composites, where these terms describe the fracture characteristics of the fibre and matrix respectively and in this review this general classification will be followed. The merits and disadvantages of these systems are briefly reviewed in the following sections.

2.1 Ductile-Ductile Systems

The reinforcing agent has to provide high strength at high temperatures, and therefore various refractory metal wires were considered in the early work, including molybdenum, niobium and tungsten [Table-3]. Molybdenum and niobium wires were soon found to react quite rapidly with nickel and its alloys at the temperatures used for fabrication or engine service and were therefore rejected. Only tungsten has remained as a viable candidate. Hard drawn tungsten or thoriated tungsten wire, of the type used in electric light bulb filaments, became the predominant reinforcement because of their low cost and availability, although some developmental grades of tungsten - rhenium and tungsten-rhenium-hafnium-carbon were also considered (9,10,12). Reinforcing wires were generally of large (100-500 μm) diameter.

The matrix alloy should generally be of low strength and high formability, and be compatible with the reinforcing agent in terms of minimum interface reactions and thermal expansion differences. It should also be oxidation and sulphidation resistant in order to withstand the aggressive engine operating environment and to protect the highly reactive reinforcing wires. Various nickel and cobalt base alloys were investigated for this purpose as indicated in Table-3, with emphasis placed on nickel base alloys.

Fabrication methods included electro-plating or vapour plating (8,18), liquid phase infiltration (6,11,22), cold pressing plus sintering (4,23), slip casting plus either sintering or HIP (5,12,16), hot pressing (4,13,22,23,26,28), hot isostatic pressing (16) or either hot forging or extrusion (17,19,27).

Demonstration programs very quickly ran into difficulties. Several studies showed that interface stability could be a problem, and that detrimental interactions between fibres and matrices could occur during either the initial fabrication of the composite or during high temperature

exposure to temperatures in the range 900-1100 C, where these composites would be required to operate. For example, molybdenum and niobium wire reinforcements were found to be severely attacked by nickel base superalloy 713C during the casting process, and several diffusion barrier coatings, including tungsten, alumina and various self-forming oxides were investigated (22). It was concluded that these coatings, especially alumina, were effective diffusion barriers for both molybdenum and niobium wires provided they remain physically intact during processing. Penetration depths of only about 2 μm were reported for as-cast tungsten reinforced nimocast 713C alloy, while depths of the order of 5-6 μm were observed after 600 hours at 1100 C (22).

However, subsequent work (8,17,18,24) showed that such interactions could lead to recrystallization in the tungsten wire with a resultant loss of strength. Other work showed serious problems of thermal fatigue during severe thermal cycling, indicating that interface strengths were insufficient to withstand the thermally induced stresses developed (10) and that loss of ductility could occur below the ductile - brittle transition temperature of 150-370 C for tungsten wire (12).

It was generally believed that refractory wire reinforced superalloy matrix composites would have considerable potential for applications in advanced gas turbine engines. The data thus far obtained indicated a potential of use temperatures of 1260 C and 1150 C for composites with and without diffusion barrier coating on the reinforcing wires respectively. Density normalized 1000 hours stress rupture values at 1090 C for tungsten wire reinforced superalloy matrix composite specimens were over four times those for conventional superalloys and twice those for the best published values for directionally solidified eutectics [Figure-2]. The potential density normalized 1000 hours stress rupture values for refractory wire reinforced superalloy composites using diffusion barrier coated wires could be from four to six times the density normalized values for directionally solidified eutctics at 1090 C [Figure-3].

2.2 Brittle-Ductile Systems

The initial interest in systems of this type was due to the very high strengths of ceramic fibres and whiskers, which were well above those of the bulk forms of these materials. Other properties such as high modulus, good strength at elevated temperature, low density and excellent oxidation and corrosion resistance combine to make ceramic fibres particularly attractive as reinforcing agents.

Weeton and Signorelli (5) reviewed the work performed at NASA. It indicated that a wide range of ceramic fibres and whiskers including silicon carbide, aluminium oxide, zirconium oxide, hafnium oxide and uranium dioxide, were being considered as reinforcing agents in matrices such as nickel base superalloys, tungsten, columbium and tantalum. The work focused on the problem of producing high strength ceramic fibres of sufficient length to act as reinforcement in metal matrices. Two methods were discussed, the first involving multiple co-extrusion of ceramic particles embedded in a metal matrix, and the second involved the expulsion of a liquid oxide through a small diameter orifice. Problems were reported for both techniques and the work was continued (5).

Restall et al. (22) studied ceramic reinforcing materials including various grades of silicon carbide rod, fibres and whiskers, hot pressed polycrystalline rods of silicon nitride, silicon nitride

whiskers, saphire rods, polycrystalline alumina and single crystal alumina rods in pure nickel, and nickel alloy matrices, such as Nimocast 713 C, Nimocast 75 and Nimocast 258. All of these fibres, with the exception of alumina, were found to be severely attacked during either the casting process, or after subsequent exposure at 1100 C (22). For example, it was found that silicon nitride rods developed interaction zones of about 50 μm in Nimocast 75 after 50 hours at 1100 C, and silicon nitride whiskers could be completely destroyed after 50 hours at 1000 C. Silicon carbide rods developed about 40 μm interaction zone in Nimocast 713 C after 20 hours exposure at 1100 C, while silicon carbide fibres and whiskers were totally dissolved in Nimocast 75 and Nimocast 713 C during the casting process. In contrast it was found that alumina formed an interaction layer only to a depth of approximately 6 μm (maximum) with Nimocast 713 C after 100 hours exposure at 1200 C and about 5 μm after 300 hours at 1100 C.

Carbon and silicon carbide fibres were also investigated as reinforcing agents in heat resistant matrices such as nickel and cobalt. However, the poor oxidation resistance of carbon fibres and the reactivity of silicon carbide fibres with most metals at high temperatures have been the main problems in the use of these fibres for high temperature composites. An excellent state-of-the-art review on carbon fibre reinforced metals covering pre 1975 status was presented by Baker (14). These problems will be further discussed in later sections.

2.3 Ductile-Brittle Systems

Ceramics such as silicon nitride and silicon carbide are also candidates for use in gas turbine engines when processed in bulk form. The processing and properties of these materials are reviewed elsewhere in detail (37).

Hot pressed silicon nitride, for example, is a leading candidate for turbine in-let guide vane applications because of its very good thermal shock resistance, but it has not been used because of its relatively poor impact strength. It is not surprising then that some early work was performed to investigate the improvements in impact properties that might be obtained by introducing metallic reinforcement to silicon nitride [Table-5] (28). The concept was to introduce an energy absorption mechanism via fibre pull-out and, at the same time, to reduce the free crack propagation distance in the brittle matrix so that only small fragments would break out of the vanes on impact rather than large pieces which might lead to catastrophic results.

Composites with ceramic matrices such as Al_2O_3, HfO_2, ThO_2, Mullite, SiO_2, zircon and Glass (33-36) with tungsten and molybdenum wire reinforcement were investigated to improve the work of fracture over the matrix material. It is reported that thermal shock produced microcracking in the matrix and severe oxidation of tungsten and molybdenum wire occured in microcracked systems when exposed to temperatures higher than 700 C in air. Fracture energy of about 12% molybdenum fibres in alumina matrix was reported to be 250 times as large as that for pure alumina (35). Flexural strengths of Mo/mullite, W/mullite and W/zircon composites were found to be higher: 25, 28 and 13 percent respectively as compared to their respective matrices (34).

Only one research program prior to 1975 was found on tungsten wire reinforced silicon nitride, and follow-on work on a similar tantalum wire reinforced system (28). The Charpy impact

strengths of W/Si_3N_4 composites were up to nine times higher than for the non-reinforced Si_3N_4 at 1300 C, but the room temperature properties were not improved. This was attributed to the presence of a brittle silicide reaction product at the W/Si_3N_4 interface and the notch sensitivity of W and, consequently, this system was abandoned. However, a much more favourable response was obtained with tantalum wire reinforcement in a matrix consisting of $Si_3N_4 + 10\%Y_2O_3$. The Y_2O_3 was used as an additive in place of MgO, which is the normal additive used to improve densification.

Ta/Si_3N_4 composites were prepared to 99+% theoretical density by a pseudo-isostatic pressing technique at 1750 C. Sufficient ductility was retained in the tantalum wires to allow them to deform on impact without breaking, thus initiating interfacial splitting and with resultant matrix shattering. The modulus of rupture in these composites at 1300 C was 351 MPa compared to 241 MPa for a similar composite consisting of the $Si_3N_4 + 5\%MgO$ matrix, and 165 MPa for the same non-reinforced matrix. Ballistic impact tests at 1300 C showed that the threshold energy below which no damage occured upon impact was of the order of five times greater than for unreinforced Si_3N_4. Creep rates at 1300 C and 103 MPa for the tantalum reinforced composite and non-reinforced $Si_3N_4 + 10\%Y_2O_3$ were similar, and an order of magnitude less than for the $Si_3N_4 + 5\%MgO$ system, with or without a reinforcement. Thermal fatigue and thermal shock properties for these composites also looked promising (28).

The results presented in this paper (28) indicate that metal wire reinforced ceramics have substantial potential for high temperature use, and that more extensive research into alloy systems, fabrication methods and mechanical properties is warranted. The work is particularly significant in terms of conserving critical and strategic elements since the metal reinforcement represents only 25-30 volume percent of the total system, while the remaining material is potentially a relatively inexpensive and abundant material. With the introduction of less exotic reinforcing fibres such as stainless steels, or other metallic fibres, ceramic matrix composites would be even more attractive.

2.4 Brittle-Brittle Systems

The most widely studied brittle fibre reinforced brittle matrix composites belong to the carbon - carbon system. It has been known in the past that certain materials such as carbon and SiC have superior mechanical properties in fibre form as compared to bulk form. Graphite is an attractive material for high temperature applications due to its high sublimation temperature, strength improvement at elevated temperature, thermal stress resistance, high heat of ablation and chemical inertness. With the commercial introduction of carbon fibres, the concept of reinforcing bulk carbon with carbon fibres proceeded very rapidly. In a comprehensive literature review on carbon-carbon composites (30), it is well illustrated that the tensile strength consistantly increases from room temperature to about 1650 C in felt/CVD and short fibre/carbonized pitch composites. Above 1650 C, the trend on tensile strength depends on the carbon-carbon system and is mixed. Compressive strength of these composites also behaves in a similar way to tensile strength. The main problem is the poor oxidation resistance. However, it is reported (30) that NASA has developed inhibitors giving carbon-carbon composites a multiple re-use capability (>25 cycles) at 1400 C and a limited re-use capability at 1800 C.

Other brittle-brittle composites investigated prior to 1975 included carbon and zirconia fibres in various glass, magnesia and alumina matrices [Table-6] (29,31,32). Both continuous and discontinuous fibres were studied in ceramic matrices. Composites containing 35-45 volume percent fibres were produced by hot pressing of premixed powder matrices and fibres in graphite dies. It was concluded (29) that, in hot pressed carbon fibre composites, thermal stresses resulting from a mismatch in thermal expansion coefficients gave rise to a cracked matrix in magnesia, alumina and soda lime glass composites, but not in pyrex or low expansion glass ceramics. The work of fracture and thermal shock resistance significantly improved in all composites as compared to their respective matrices. Furthermore, it was observed that the behaviour of composites at elevated temperatures appeared to be limited by oxidation of the fibres. Carbon fibre reinforced glasses maintained their strengths in an inert atmosphere at high temperatures (>500 C), however heating in air caused oxidation of the carbon fibres which resulted in the degradation of the composite strength. Composites of zirconia fibres in magnesia showed little change in strength with temperature up to 1500 C (29).

3.0 CURRENT STATUS

In the eleven years since 1975 at least 92 additional papers on artificial high temperature composites have appeared and these are summerized in Tables 7-10. These tables do not necessarily provide a complete review, but they do indicate that the level of interest and activity is not declining. A review of the systems investigated reveals that work has continued on metal-metal systems [Table-7] ($\approx$ 39 papers), ceramic-metal systems [Table-9] ($\approx$ 6 papers), metal-ceramic systems [Table-10] ($\approx$ 3 papers) and several reports ($\approx$ 32 papers) appeared on systems containing entirely brittle materials, including various ceramics, glasses or carbon compounds [Table-8].

Perhaps the most significant development in the past twelve years has been the systematic characterization of individual fibres and matrix constituents (45,47,50,56,64,70,74). These studies have been amply supported by studies of interfacial reactions and diffusion barriers (40,47,55,56,64, 72,73,78,113,116,117), processing studies (45,49,54,59,62-67,74,78), mechanical property studies (49,50,52,53,61,64,70,74,79,110,114,116), technical reviews (38,41.57,58,60,67,75,97,98) and cost studies (66,87,89,90).

In a review by Warren (37) several material types were identified as having sufficient strength to qualify for high temperature structural use. A particular point to notice is that several materials, including graphite, have much higher strength in fibre form than in bulk form and, therefore, would be attractive as reinforcing agents. Even when combined with bulk carbon to form a carbon-carbon composite, they retain very high tensile strengths, even at temperatures above 1500 C, when most metals would be molten. However, poor oxidation resistance of carbon-carbon composites has prevented their use in gas turbine structural components. Other outstanding materials identified by Warren (37) include Si_3N_4 and SiC, which are candidates for use either as reinforcing fibres or as matrix materials. As noted previously, the outstanding oxidation resistance of Si_3N_4 make it particularly attractive as a matrix phase, provided its brittle fracture characteristics can be either modified or accomodated through design inovations. The combination of graphite fibres with silicon nitride matrix looks immediately promising, and will be discussed later.

3.1 Ductile-Ductile Systems

The development of refractory metal wire reinforced metals has continued vigorously in the past twelve years. About 42 papers investigating various aspects of ductile-ductile composites have appeared and they are listed in Table-7. Particular attention has been paid to refractory wires and their fabrication (40,45,47,50,56,64,75), optimization of the matrix alloy composition (40,47,50,52,53,56,64,74,110),fabrication processes (54,59,62-67,70,74,78), fibre/matrix interaction, diffusion barrier technology (40,47,49,55,72,73,78,107,110,113,117)and mechanical properties characterization (49,52,53,61,64,70,74,79,110,114,116). In the following sections these aspects are reviewed separately for ductile-ductile composites.

3.1.1 Reinforcing Filaments

As mentioned in Section 2.1, molybdenum and niobium base wires were shown to react severely with the matrices, thus their use as reinforcing agents has been very limited. Only one paper has appeared in the past twelve years reporting the use of $Mo-TZM$ wires with a $FeCrAlY$ matrix (58). Most of the work reported in the past decade has utilized wires of tungsten or tungsten base alloys for reinforcement purposes [Table-7]. Hence, these composites are now commonly referred to as tungsten fibre reinforced superalloys or TFRS.

Investigations to produce higher strength wires have been successful to a considerable degree. Tungsten or dispersion strengthened (ThO_2) tungsten has remained the most widely examined material, but other tungsten base alloys, such as $W-Hf-C$ and $W-Hf-Re-C$, were developed with strengths over sixteen times those of superalloys and twice as high as that of commercial lamp filaments, [Figure-4]. The composition and thermo-mechanical processing of the $W-Hf-Re-C$ wires had not been optimized. Thus the properties demonstrated so far are merely indications of the first generation of the wires. Considerable further improvement in properties can therefore be projected.

3.1.2 Matrix Materials

Matrix alloy also plays an important role in the final properties of the composites. The matrix requirements are more complex since there has to be a trade-off between conflicting parameters. Some of the more important requirements are:

1. Compatibility with fibres - both chemical and physical. The development of suitable diffusion barrier coating or matrix alloy should reduce the importance of this requirement.

2. Oxidation resistance at elevated temperatures, as the matrix also serves the purpose of protecting the highly oxidation prone reinforcing wires.

3. Diffusion bondability - all solid state fabrication processes require ease of diffusion bonding, and chemical composition may have significant effects on sintering of powders and on diffusion bonding of sheets.

4. Ductility for good impact resistance.

5. Good thermal fatigue properties.

Several alloys have been investigated as matrices in the past twelve years and are listed in Table-11 along with their chemical compositions. The alloys investigated as matrices can be generally divided into three groups:

1. Nickel base alloys (40,50,52,55,64,68,77,107, 110,113,114,116,117)

2. Cobalt base alloys (47,54,56,74,110)

3. Iron base alloys (40,41,49,50,53,57-60,62,63,65,66,70,72,75,78,79,87,89,110,117)

Almost all nickel base superalloys, such as Inconel 718, Inconel 600, Hastelloy X, Nimonic 80A, IN 102 and including pure nickel, have been used as matrices. Several experimental grades of nickel base superalloys were also investigated for the purpose of matrix optimization. *NiCrAlY* showed considerable potential compared to other nickel base superalloys. Cobalt base alloys such as MAR M 322, along with some of its modifications, and MAR M 302 were also used as matrices.

Perhaps the most significant improvement in the matrix materials has occured through the use of *FeCrAlY*, which at present appears to be the most promising candidate for high temperature applications. This alloy has received close attention as matrix material due to its outstanding oxidation resistance along with the potential to perform satisfactorily, without protective coating, in an engine environment. It is relatively soft and therefore can be easily used as matrix material, has a high melting point, and appears to be compatible with tungsten thus potentially eliminating the need for fibre/matrix diffusion barrier coatings.

3.1.3 Fabrication Processes

Fabrication processes for ductile - ductile composites included both liquid and solid state processes and in some cases, secondary operations such as hot forging or hot swaging were also applied.

Solid state diffusion bonding techniques such as hot pressing or hot isostatic pressing have remained the most widely used processes for the fabrication of ductile - ductile composites (49,50,52,53,54,57,58,61,63-66,70,72,75,79,107,113). Generally in these techniques, the reinforcing wires are collimated by drum winding with a sacrificial polystyrene binder to form a mat. These mats are then cut to size and sandwiched between either foils or powder cloth of matrix alloy of appropriate thickness. Powder cloth is produced by blending a small quantity of organic binder (usually teflon) and warm rolling to produce high density and handleable sheets. Sheets of matrix

powder as thin as 0.0127 cm. can be readily produced by this method (16). Sandwiched powder cloth matrix and collimated reinforcing wires of a desired number of plies can then be consolidated by either hot pressing under controlled atmosphere or by hot isostatic pressing. The organic binders used are completely removed under dynamic vacuum during the heat up cycle.

Other solid state composite fabrication processes included cold compaction of matrix powder or sheets with reinforcing wires, followed by either sintering and/or hot swaging (55,62,78,116). Cladding of reinforcing wires with matrix tubes without any binders, and then hot isostatic pressing of these bundles has also resulted in acceptable ductile-ductile composites (63,70,72).

Electroplating was generally used to produce nickel coatings on tungsten wires for wire/matrix interaction studies (73,114,117).

Liquid phase fabrication processes included investment casting under vacuum (47,56,57,74) and vacuum liquid infiltration of wires with the matrix alloys (68,77).

Perhaps the most significant acheivement in the past decade is the development of the fabrication processing of complex, hollow, air cooled aerofoil section of turbine blades. The process shown schematically in Figure-5 has been used to fabricate a prototype first stage turbine blade. The process uses diffusion bonding of mono-layer composites along with steel core plies and unreinforced cover skin plies at the inner and outer surfaces. After diffusion bonding, the steel core is leached from the aerofoil leaving a hollow configuration. An impingement cooling insert can be inserted to improve the interior cooling aerofoil path. Although this process has been demonstrated successfully, the larger effort to develop manufacturing process technology is yet to come.

A further achievement has been reached as part of the prototype turbine blade fabrication, which addresses the concern of component density and weight for TFRS composites. The normalized strength/density values of TFRS are used for comparison with superalloy properties for components, [Figure-4]. Since tungsten is twice the density of nickel, the concern has been that while the strength/density values are high, the component weight is also high and this affects the requirements for other components such as turbine discs. However, by varying the fibre content along the span length of the aerofoil to match the stress and temperature requirements and by varying the hollow blade wall thickness, blade weight can be very similar to that of superalloys (38).

3.1.4 Wire/Matrix Interactions and Diffusion Barriers

High temperature compatibility of fibres with matrices has remained a source of concern in ductile-ductile composites. As mentioned earlier (Section 2.1), due to excessive interactions, molybdenum and niobium base refractory alloy wires have been almost compeletely abandoned for use as reinforcing agents. Only tungsten base wires have remained viable from the high temperature compatibility standpoint, although serious problems were also reported with some matrices.

A model system comprised of tungsten wires embeded in a copper matrix was used to study the degradation mechanism in tungsten wires. This system was selected because copper and

tungsten are mutually insoluble, because copper wets tungsten and because copper has much lower strength and modulus than does tungsten. When unidirectionally reinforced, this system observes the law of mixtures very closely. However, when nickel, cobalt or zirconium were individually alloyed with the matrix (copper), the properties of tungsten wires were degraded even though the alloying additions were only about 5-10 volume percent (4). This degradation was shown to be the result of a distinct recrystallization zone formation on the wires, and the thickness of the recrystallized zone increased as the volume percent of nickel, cobalt or zirconium was increased in the matrix. The reaction with cobalt additions was found to be the most severe, thus indicating that the presence of certain elements in the matrix could lead to composites with lower than expected strengths.

It was observed earlier that nickel induces recrystallization in tungsten. Montalbano et al. (8) showed that nickel, aluminium, manganese and palladium lowered the recrystallization temperature of doped tungsten from 2000 C to 1000 C, while many other elements lowered it to a lesser extent.

It is generally believed that nickel diffuses through short circuit paths in the recrystallized grains and across the recrystallization interface into sinks associated with high defect density within the fibrous grains. Jones (73), in order to elucidate the mechanism, studied the nickel activated recrystallization of doped tungsten and $Mo - TZM$ by using an ion probe mass spectrometer. He suggested that the movement of recrystallization boundary occurred by the selective grain growth, and a close correspondance between nickel penetration and the depth of recrystallization was observed.

Kozma (117) studied the effects of heat treatment on $W - Ni$ and $W - Fe$ interfaces. He observed that uncoated tungsten wires, when exposed to high temperature, underwent only recovery and growth of the average grain diameter from 0.5 μm to about 1 μm, while the activators (Ni, Fe) brought about secondary recrystallization resulting in an average grain size of 10-20 μm depending on the temperature of the anneal. The advance of the recrystallization boundary with both iron and nickel was found to be a square root function of the annealing time [Figure-6]. It was also found that tungsten grains contained both nickel and iron in low concentrations with a homogeneous distribution. However, the nickel concentration increased from 0.05 atomic percent at 1350 K to 0.25 atomic percent at 1900 K, thus providing a further evidence of a diffusion controlled mechanism. It was further postulated that due to negligible rate of lattice diffusion at the temperatures used, the formation of the W/Ni and W/Fe solid solutions cannot be explained with diffusional alloying. However, it was proposed that they are produced by co-precipitation of tungsten and nickel or iron, but this mechanism requires the presence of a new phase formed by the activators. Indeed, high magnification scanning electron microscopy of specimens fractured after high temperature exposure has verified the existence of a new phase after the onset of recrystallization. Further, nickel produced a thicker and more continuous film of the new phase at the grain boundaries as compared to iron. The presence of this new phase at the recrystallized grain boundaries further explains the difference in creep and fatigue properties of recrystallized and un-recrystallized tungsten wires.

Warren and Anderson (114) studied the effect of nickel coatings on the creep properties of tungsten wires. They showed that nickel coated tungsten wires, which were recrystallized prior to creep testing, exhibited several orders of magnitude increase in secondary creep rate and a corresponding reduction in fracture time as compared to uncoated wires. This degradation was attributed to the nickel induced recrystallization of tungsten wires.

Cobalt, as mentioned earlier, also has a detrimental effect on tungsten (4). However, attempts were made to use MAR M 322 alloy as matrix due to its high melting point and high tungsten content. Modification of the alloy by increasing its tungsten content from 9 to 25 weight percent showed that filament/matrix interactions could be reduced significantly (74). Interaction zone thickness increased from 8 μm in 'as cast' composite to only about 38 μm in specimens exposed to 1150 C for 1000 hours and which contained 25 percent tungsten in the matrix (74).

Iron base matrices have also shown interface interactions with tungsten fibres. In a study of reactions between thoriated tungsten fibres with iron base powder matrices (78), it was reported that pure iron induced partial fibre recrystallization and a boundary inter-metallic layer was formed after exposure at 1400 C for 1 hour. Binary iron base powders also recrystallized tungsten fibres and a layer of about 12-15 μm thick of brittle, comparatively hard inter-metallic compounds was also formed at the fibre/matrix boundaries. It was, however, concluded that iron base powder alloys can be successfully used as matrices, and the composition can be chosen so that the matrix forms no inter-metallic compounds. Further it was concluded that the possible reactions between tungsten and iron base matrices may include dissolution of tungsten fibres, formation of inter-metallic compounds and recrystallization of tungsten fibres if sufficient care was not taken in the proper selection of the matrix alloy.

Kim et al. (49) reported that inter-metallic compounds were formed when plain carbon steels (AISI 1010 and 1095) were used as matrices with tungsten fibres. As tungsten is a strong carbide former, then depending on the carbon content of the matrix, a variety of complex carbides can be formed at the interface in the temperature range of 650-1300 C.

Warren et al. (72) used standard stainless steel of AISI type 304 as matrix with $W - 2\%ThO_2$ reinforcing filaments. They also noted that the reaction zone thickness increases linearly with the square root of time, and increasing temperature increases the rate of increase of the zone thickness. The reaction zone composition was found to be 55% W, 33% Fe, 9% Cr and 3% Ni, and it was deduced that the zone consists of either Fe_3W_2 or Fe_7W_6 compounds, which are stable in $Fe - W$ system. Recrystallization of the tungsten wire was also observed but the degree of recrystallization was much smaller than that observed with nickel base matrices.

Generally, it can be argued that iron base matrices are more compatible with tungsten as compared to nickel base matrices mainly due to:

1. The solubility of tungsten is much lower in iron than in nickel (10 and 38 percent respectively).
2. Iron is less active in promoting the recrystallization in tungsten.
3. The compounds formed in $Fe - W$ are much more stable at elevated temperatures than any $Ni - W$ compound.

Consequently much more effort is being expended in the development of iron base matrices for high temperature composites.

As tungsten has shown interaction problems with all three major matrix alloy groups (Ni, Co, and iron alloys), and because matrix modifications to improve compatibility have not

proved to be very successful, incorporation of diffusion barrier coatings on tungsten wires were also investigated. The major requirement for the diffusion barrier layer is to hinder or preferably to prevent the inter-diffusion between fibre and matrix. The barrier layer must also be stable at elevated temperatures, and should be compatible elastically, and should fullfil thermal expansion requirements for both fibre and matrix.

Several diffusion barriers were developed including oxides, carbides and nitrides of hafnium, zirconium, titanium, tantalum, aluminium and chromium. These thin coatings were applied on wires either by chemical vapor deposition or by activated reactive evaporation (rf sputtering) techniques.

Mazzei et.al. (40) used commercially available tungsten and tungsten containing 1-2% thoria with and without HfN diffusion barrier coatings in Hastelloy X, Haynes 188 and $FeCrAlY$ matrices. They reported that without HfN diffusion barrier coating, Hastelloy X, Haynes 188 and $FeCrAlY$ developed 17, 26 and 37 μm thick reaction layers respectively in the wire after exposure to 1150 C for 144 hours. Similar exposure of composites containing 3-4 μm thick HfN diffusion barrier coatings produced no interaction layer in Hastelloy X and $FeCrAlY$ matrices, while the composite containing Haynes 188 as matrix showed a reaction layer of only 8 μm thickness. However, a reaction layer of less than 0.5 μm thickness was observed between the coating and the matrix. Nevertheless, superior creep properties were observed in composites with HfN diffusion barrier coating as compared to composites with uncoated wires. The increase in creep properties was attributed to the absence of recrystallized zones in the diffusion barrier coated tungsten wires.

Ahlroth (55) studied the use of 1-2 μm thick rf sputtered TiC and TiN diffusion barrier coatings to avoid deleterious reactions between tungsten wires and nickel alloy matrix. It was concluded that these diffusion barriers retard but do not eliminate completely the deleterious interaction between tungsten fibre and nickel matrix. The reaction zone thickness was found to decrease from about 30 μm in uncoated wire composites to less than 1 μm in composites containing coated tungsten wire after 114 hours exposure at 927 C. Further, it was noted that the destruction of the diffusion barrier layer is initiated by the diffusion of nickel through the coating, hence particular attention should be paid to the coating process to optimize the internal structure of the diffusion barrier coating.

In a subsequent study, Ahlroth and Kettunen (116) showed that the diffusion barrier coating method and hence the structure of the diffusion barrier coating does have a significant influence on its high temperature characteristics. Diffusion barrier coatings of TiC, TiN and $TiC + TiN$ were applied on tungsten wires using both conventional methods i.e chemical vapor deposition and reactive rf sputtering technique. Composites were prepared under similar conditions using uncoated, CVD coated and rf sputter coated tungsten wires with nickel matrix. It was shown that after 114 hours exposure at 927 C, the thickness of the diffusion zone measured was 30, 10, 5-20 and less than 1 μm in uncoated, $CVD - TiC$, $CVD - TiN$ and rf sputter coated TiC or TiN or $TiN + TiC$ tungsten fibre/nickel composites respectively. This indicated that the rf sputtering technique produced a better coating than the chemical vapor deposition method, however, no attempt was made to analyze the internal structure of the coatings produced. It was also concluded that both TiC or TiN coatings slightly improve room temperature tensile properties and the endurance limit is not affected. However, fatigue properties at higher stress amplitude are slightly decreased, although above 650 C, all the fatigue properties were improved in composites

containing diffusion barrier coatings.

Lee et.al. (113) studied 1-4 μm thick coatings of ZrC, ZrO_2, HfC, HfO_2, TaC, Al_4C_3 and TiC on tungsten fibre of 500 μm thickness in a matrix of nickel. Both diffusion barrier coated and uncoated tungsten fibre/nickel matrix composites were exposed to 1150 C up to 200 hours. It was observed that in uncoated tungsten wire/nickel composites, a compound layer was formed at the fibre/matrix interface before 50 hours of exposure. This layer then began to diffuse into the nickel matrix with an increase in exposure time, and was eventually decomposed after 200 hours exposure. Diffusion zone thickness in the vicinity of the compound layer was detected to increase with exposure time and recrystallization of the tungsten wires was also observed. In contrast to the uncoated tungsten wire/nickel composites, most of the coated tungsten wire/nickel composites appeared to be relatively free from the detrimental interactions between tungsten wire and the nickel matrix. Among all the barrier coatings studied, zirconium carbide and zirconium dioxide coatings were found to be the most effective. It was also shown that the bending strength of the ZrC or ZrO_2 coated tungsten wire/nickel composites, exposed to 200 hours at 1150 C, exhibited no significant change, while the bending strength of the uncoated tungsten wire/nickel composites was reduced from 126 kg/mm^2 to only 49 kg/mm^2. This drastic reduction in the bending strength after high temperature exposure was attributed to the secondary recrystallization of the tungsten wires. As the hot pressed bending strengths of ZrC or ZrO_2 coated tungsten wire/nickel composites (68 and 82 kg/mm^2 respectively) were reported to be lower than uncoated tungsten wire/nickel composites (126 kg/mm^2), an explanation was offered in terms of differences in the fabrication conditions.

Umekawa et.al. (107) examined the effects of diffusion barrier coatings on interfacial reactions in tungsten/nickel and tungsten/316L stainless steel composites. Oxides, carbides and nitrides of aluminium, titanium, chromium, zirconium and tantalum were investigated as diffusion barriers with 1-7 μm thickness and were applied on tungsten wires by using the activated reactive evaporation technique. Again ZrN and ZrO_2 coatings were found to be the most effective diffusion barriers. It was shown that in stainless steel matrix composites without any diffusion barriers, a reaction zone thickness of 70 μm was observed after 1200 C exposure for 200 hours. On the other hand, composites having ZrN or ZrO_2 diffusion barrier coatings showed very little or no reaction zone. High temperature impact and bending properties were also shown to improve significantly in composites with ZrN or ZrO_2 diffusion barrier coatings, presumably due to the absence of a recrystallized zone on the tungsten wires.

It is well established that various diffusion barrier coatings are effective in preventing detrimental interactions between tungsten fibres and matrices; this technology, however, is still in its infancy. A considerable amount of work is required on:

1. The characterization of the barrier coatings both physically and chemically.
2. Optimization of the coating processes.
3. Optimization of the coating thicknesses.
4. Characterization of the bonds and interaction between fibre/coating and coating/matrix interfaces and their effects on the composites.

Although high temperature exposure of the composites containing barrier coatings have shown their effectiveness, thermal fatigue properties of these composites are still not fully evaluated. Most of these diffusion barrier coatings are brittle in nature and it was demonstrated that a secondary fabrication operation of isothermal forging of composite preforms could lead to separation and cracking at the barrier/wire interface (54). Thus, thorough and careful evaluations of the diffusion barrier coatings and their effects on mechanical properties, forming characteristics and in-service operating characteristics of composites are needed before they can be used with confidence in engineering systems.

3.1.5 Mechanical Properties

For detailed design of turbine engine components, such as turbine blades, the properties of tungsten fibre reinforced superalloys (TFRS) must be well characterized. Unfortunately TFRS properties cannot be as easily summerized as can superalloy properties. The reason being that TFRS are laminated structures and are not simple materials. Literally thousands of valid permutations of fibre diameter, volume percent and fibre angle versus ply sequence exists for even simple TFRS laminated structures. The overwhelming quantity of variations makes thorough characterization of each variation impossible. Moreover, the properties of TFRS laminates are highly geometry dependant; for example, merely changing the width of an angle plied test panel can drastically affect the strength properties. Therefore, unlike the situation for superalloys, tests conducted on simple TFRS laboratory specimens can give grossly misleading indications of the component performance. Consequently, TFRS components must be custom designed for each specific application and then tested in a form as close to the component geometry as possible. Furthermore, the suitability of TFRS for a specific application should rather be determined by individual design, analysis and testing and not by direct comparison with superalloy properties.

In Table-12, material properties important in turbine blade applications are listed, and in Table-13, minimum property data needed to design turbine blades for developmental engines is shown. It will be seen in the following sections that, so far, all these properties are not determined for any single composite, although it has been successfully demonstrated that turbine blades of $W - 1\%ThO_2/FeCrAlY$ can be fabricated. Despite the fact that mechanical property data on TFRS is not complete, in the following sections an attempt is made to present the available data in a systematic order.

3.1.5.1 Tensile Properties

The tensile properties of TFRS, determined experimentally since 1975, are listed in Table - 14. It is seen that the tensile data obtained thus far is not complete for any single TFRS. In most of the cases, even tensile modulus is not reported and the tensile properties are not measured in the full temperature range in which parts made from these composites are expected to operate. In Table-14, the available tensile properties are listed in a systematic order, including the major variables of the composites. Thus the tensile properties of these composites can be compared with the matrix alloy properties to assess the effects of reinforcement, and a general comparison can also be made between the different composites themselves.

It is generally observed that the tensile properties of TFRS at room temperature are inferior to those of the matrix alloy, due mainly to the flaw sensitivity and brittleness of the reinforcing tungsten filaments at low temperatures. As the test temperature is increased above the ductile/brittle transition temperature (DBTT) of tungsten filaments, the properties of the TFRS improve considerably over the matrix materials. For example, the ultimate tensile strength of $W - 2\%ThO_2$/MAR M 200 composite containing 50% unidirectional reinforcing filaments at 1090 C is reported to be 595 MPa, as compared to only 213 MPa for MAR M 200 alloy at the same temperature. For comparison, when these tensile strength values are divided by their respective densities, specific strength values of $2.49 \times 10^4 N.m.kg^{-1}$ and $4.33 \times 10^4 N.m.kg^{-1}$ are obtained for un-reinforced MAR M 200 alloy and $W - 2\%ThO_2$/MAR M 200 composite respectively. Thus the composite showed 1.74 times better specific strength at 1090 C than the base alloy. Similarly, cobalt base alloy MAR M 322 E shows ultimate tensile strength of 117 MPa when tested at 980 C, but when reinforced by about $40\%W - 2\%ThO_2$, this value is increased to 537 MPa. Again if these values are divided by their respective densities, it can be seen that 40% reinforcement produces about 3.17 times higher specific strength as compared to the base alloy alone at 980 C. Composite made with iron base matrix $FeCrAlY$ showed the best UTS value of 607 MPa when tested at 1093 C, and on a density normalized basis this composite offers specific strength at least twice as high as that of the best superalloy at that temperature. An indication of the mechanical stability at high temperature was also provided when the ultimate tensile strength of $W - 1\%ThO_2/FeCrAlY$ stayed the same before and after creep testing at 1093 C for 990 hours.

3.1.5.2 Stress Rupture Properties

Stress rupture properties are measured to provide an indication of mechanical stability under sustained load at high temperatures. In Table-15, TFRS data reported since 1975 on stress rupture properties are summerized. Sometimes stress rupture data is also presented as a plot of applied stress versus the Larson-Miller parameter "P", which is calculated as:

$$P = T \times 10^{-3}(20 + \log t)$$

where:

P - Larson-Miller parameter
T - Temperature in degrees Kelvin
and t - Rupture time in hours

In Table-15, Larson-Miller parameter (P) is given for each composite data set along with specific stress rupture (rupture strength/density) value for comparison. For stress rupture conditions of 100 hours at 1093 C and 1000 hours at 1093 C, the Larson-Miller parameter has the values of 30.05 and 31.4 respectively.

It can be seen in Table-15 that at a similar value of "P", TFRS stress to rupture and specific stress rupture values are far superior to either the matrix material itself or to that of the best superalloy available. For example, cobalt base alloy MAR M 322 E showed stress to rupture value of 48 MPa and specific stress rupture value of $0.53 \times 10^4 N.m.kg^{-1}$ at a "P" value of 29.9. On the other hand composite made from the same matrix along with about $43\%W - 2\%ThO_2$ wires

had stress to rupture value of 228 MPa and specific stress rupture value of $1.72 \times 10^4 N.m.kg^{-1}$ at a "P" value of 30.07. Similar increases are also evident from Table-15 for other composite systems.

In Figure-7, a comparitive plot of density normalized stress to rupture values versus the Larson-Miller parameter is shown. For comparison the best superalloys and γ/γ' - δ (directionally solidified eutectic) properties are also shown. The superiority of TFRS, especially at high "P" values, immediately becomes evident. Although the tungsten fibre has a high density , TFRS maintains a superiority over other high temperature materials when compared on the basis of specific (density normalized) strength, as is shown in Figure-7. For a 1000 hours rupture life, TFRS offers 100-185 C increase in temperature capabilty, depending upon the volume fraction of the reinforcement. Furthermore, stress rupture is a fibre controlled property and as new high strength fibres become available, further increases in the temperature capability of TFRS may still be possible.

3.1.5.3 Thermal Fatigue

Thermally induced stresses are generated in turbine blades because of temperature gradients. These gradients change with time, leading to cyclic stresses and hence potential fatigue failures, particularly at stress concentrations such as cooling holes. Superimposed on these stresses, in the case of composites, are internal stresses caused by the difference in expansion coefficients between the fibre and the matrix. This is potentially the most serious limitation on composite usefulness. Consequently, much attention is being paid to improving the resistance of TFRS to damage due to thermal cycling.

Friedman and Fleck (50) studied the thermal fatigue properties of five composites containing W filaments in matrices of Inconel 600, IN 102, Hastelloy X, Nimonic 80A and $FeNiCrAlY$. The specimens were resistively self heated in an argon atmosphere and a tensile load of about 10 MPa was applied on the specimens to avoid slipping. The specimens were heated and cooled in a three minute cycle from 450 C to 1093 C and back to 450 C. It was reported that all five composites survived 1000 cycles without any catastrophic failure. However, composites with Inconel 600 and $FeNiCrAlY$ matrices were the best in terms of dimensional stability and internal damage, although some signs of surface roughness were observed. The other three composites showed surface cracks and considerable dimensional changes.

Warren et al. (52) studied the effects of thermal cycling on composites containing about 30 volume percent $W - 2\%ThO_2$ in four matrices viz: stainless steel 321, KOVAR, Inconel 718 and Hastelloy X. Specimens were subjected to up to 3600 cycles between temperatures of 90 and 925 C. It was observed that, with the exception of KOVAR matrix composites, all others exhibited considerable plastic deformation and grain boundary cracking within 50 cycles. KOVAR matrix composites did not show any significant external change for up to 1000 cycles. Warpage and debonding was also observed when composite containing 17 volume percent $W - 2\%ThO_2$ filaments in a matrix of cobalt base alloy MAR M 322E was subjected to 500 cycles from 450 to 1093 C (47,74).

Composites with $FeCrAlY$ matrix have thus far demonstrated the best thermal fatigue behavior and show considerable future promise. The response of $W - 1\%ThO_2/FeCrAlY$ to thermal

cycling was evaluated (as mentioned in Reference 57) and found promising. Specimens containing 30 volume percent filaments were exposed to 1000 heating and cooling cycles from 22 to 1200 C. Surface roughening was observed but there was no matrix or fibre cracking after 1000 cycles and the specimens were dimensionally stable. Similar behavior was also observed by Petrasek et al. (57), even though a more severe heating and cooling cycle was used. Unidirectionally reinforced panels of 35 volume percent $W - 1\%ThO_2/FeCrAlY$ composite were shown to survive 104 cycles from 20 to 1100 C without any matrix or fibre damage (79). Essock and Machlin (58) used two types of testing to evaluate the thermal fatigue response of $W - 1\%ThO_2/FeCrAlY$. First, residual room temperature tensile strength was measured after thermal cycling between room temperature and either 1093 C or 1204 C. It was reported that, regardless of temperature, 100 cycles appears to have no effect on tensile strength or failure strain, however both decrease after 1000 cycles. The second set of tests was an in-phase temperature and stress cycle. Temperature was varied between 21-750 C, while the stress range selected was 0-413 MPa. Both unidirectional and $\pm$ 15 degree material survived 1000 cycle test with some dimensional changes.

3.1.5.4 Impact Properties

Pendulum impact tests show that composites exhibit a pronounced ductile-brittle transition around 470 C. A typical notched impact strength versus temperature plot for $W - 1\%ThO_2/FeCrAlY$ is shown in Figure-8 (57,79). Similar behavior was also reported with nickel matrix composites (50). Composites containing $W - 2\%ThO_2$ filaments in a cobalt base matrix MAR M 322E showed a continuous increase in impact energy with temperature, with a slight flattening of the curve around 315-537 C (47).

It is generally believed that the impact strength of a composite primarily depends on the matrix toughness at temperatures below the ductile-brittle transition temperature of the fibres. Thus the use of a tougher matrix alloy should provide composites with better impact properties below the ductile-brittle transition temperature (DBTT). However, above the DBTT of the fibres, the impact strength is primarily controlled by the fibres as indicated by large increases in fracture energy at these temperatures. Nevertheless, $W - 1\%ThO_2/FeCrAlY$ composites showed impact energies which are at least 57 Joules higher than the accepted minimum requirement for turbine blade materials at temperatures above 150 C (79).

3.1.5.5 Fatigue and Creep Properties

There is only a limited amount of experimentally measured data available on creep and fatigue properties of ductile - ductile composites. Only 8 papers out of approximately 42 papers have been identified on these systems. Such papers report experimentally measured properties and most of them are mainly focused on fabrication, fibre/matrix interaction or other properties.

Larson and Warren (70) reported limited creep properties of composites containing 20-30 volume percent of either lamp wire or $W - 1\%ThO_2$ in a matrix of 304 stainless steel. Creep specimens made from KOVAR matrix failed on the grips before the tests were completed. However, creep tests were carried out at 900 and 950 C in air on stainless steel matrix composites with stress

levels from 60-250 MPa. The composites exhibited classical creep behavior with primary, secondary and tertiary creep stages. At low loads the secondary creep rate decreased slightly after about 200 hours. The results were also reported in the form of a Larson-Miller type plot. It was shown that at a Larson-Miller parameter of about 27, the stress required to cause 3 percent strain with secondary creep rate was about 120 MPa and about 230 MPa for composites containing 20 and 30 volume percent filaments respectively.

Warren and Anderson (114) studied the effects of nickel coatings and matrices on the creep of tungsten wires between 900 and 1050 C. Nickel coated wires, recrystallized prior to creep, exhibited a several order of magnitude increase in the secondary creep rate and a corresponding reduction in fracture time as compared to uncoated wires. This behavior was attributed partly to the coarsening of the micro-structure and partly to nickel enhancement of self diffusion process in tungsten. Nickel coated wires, not recrystallized prior to creep, exhibited intermediate creep rates and reduced fracture strains. Based on the results of this study (114) and previous studies by the same authors (as mentioned in Reference 114), it was suggested that for tungsten fibre reinforced composites, nickel should be avoided in favor of iron in the matrix.

Essock and Machlin (58) reported the time to 1% creep for $W - 1\%ThO_2/FeCrAlY$ and compared it with other state-of-the-art high temperature materials using Larson-Miller type plots. It was shown that at low levels of reinforcement (<20 %), TFRS is about equivalent to the best of the available superalloys, and as fibre volume fraction is increased beyond 30 %, the TFRS exhibited a decided superiority in creep resistance. Petrasek et al. (57) reported that the creep behavior of $W - 1\%ThO_2/FeCrAlY$ is similar to that of directionally solidified eutectics at 1310 K. In Figure-9, a comparative plot of the creep behavior of $W - 1\%ThO_2/FeCrAlY$ and the directionally solidified eutectic is shown.

In composite materials with significant differences of thermal expansivity between fibres and the matrix, the terms thermal fatigue and low cycle fatigue are perhaps more closely related than in the case of macroscopically monolithic materials. Thermal cycling alone of unrestrained specimens can cause substantial cyclic plastic strains and can cause the matrix to undergo constant strain amplitude tension-compression fatigue. Thus for the purpose of clarification, thermal cycling data without or with a small load are presented in Section 3.1.5.3, and in this section load or strain controlled cycling, under isothermal or cyclic temperature conditions, will be reviewed.

Ahlroth (55) and Ahlroth et al. (116) reported the fatigue properties of W/Ni composites with and without diffusion barrier coatings of TiC or TiN on tungsten fibres. Although the composites contained low volume fractions of fibres (only 6 and 12%), the fatigue properties of the composites were better than those of the matrix itself at 650 C. The S-N curve of the composites fatigued at 20 C showed that at high stress amplitudes, the composites with uncoated wires had slightly longer fatigue life as compared to the composites containing coated wires, however, at the endurance limit no significant difference was observed. Increase in fatigue life, with an increase in the fibre volume fraction, was also observed.

Brentnall (79) and Essock et al. (58) reported the results of low cycle fatigue tests on $W - 1\%ThO_2/FeCrAlY$ composites. Tests were conducted with temperature cycles of 21-649 C and 21-760 C, with in-phase (load controlled) tensile stress cycles ranging from 0 to 275, 344 or 413 MPa. Both unidirectional and $\pm$ 15 filament composite were tested and were reported to

survive 1000 cycles. However, post test measurements revealed some dimensional changes without any distortion or surface cracking. Specimens with $\pm$ 15 filament orientation showed signs of necking after 1000 cycles.

High cycle fatigue tests were not performed on $W - 1\%ThO_2/FeCrAlY$ composites. However, work prior to 1975 (9) on W/Hastelloy X composites showed the fatigue life superiority of the composite over the matrix itself at all the test temperatures (RT-1000 C). On the basis of these tests, it was assumed by some authors (41,57,60) that $W - 1\%ThO_2/FeCrAlY$ composites should have adequate fatigue properties for their application in turbine blades.

3.1.5.6 Oxidation and Hot Corrosion Resistamce

Oxidation and hot corrosion resistance of TFRS are primarily dependent on the matrix. Composites with $FeCrAlY$ matrix containing fully encased reinforcing fibres are considered to be the most promising. Alloys based on the ternary $Fe - Cr - Al$ system with yitrium additions are among the most oxidation resistant alloys known. As a result they are used as oxidation resistant coatings on directionally solidified eutectics and superalloys. Therefore, the composites with $FeCrAlY$ matrix should have adequate oxidation and corrosion resistance for turbine blade application and could be used without any external coating provided the fibres are fully encased. On the other hand TFRS with other superalloy matrices may need protective coatings to survive high temperature exposures over long periods of time.

3.2 Brittle-Ductile Systems

As mentioned in Section 2.2, the initial interest in brittle-ductile composites was mainly due to extremely attractive properties of ceramic fibres and whiskers. The technology of ceramic fibre reinforced composites with low temperature matrices such as aluminium, magnesium and titanium is in a fairly advanced stage, however, very little work appears to have been published utilizing matrices capable of withstanding high temperatures. Since 1975 only six papers have been identified that report on brittle fibre reinforced metal matrix composites with high temperature potential. Consequently very little data is available and most of it is priliminary and exploratory in nature.

3.2.1 Fibres, Matrices and Fabrication Processes

In Table-9, the research activities on brittle-ductile composites, reported since 1975, are listed. It can be seen that three types of reinforcing fibres have been explored including silicon carbide, carbon and potassium titanate. The matrices included pure nickel, $FeCrAlY$, Waspalloy, Hastelloy X and Haynes 188. Fabrication processes involved electro or electroless nickel plating (44,51), diffusion bonding of mono-layer tapes (42,48) and hot pressing of powder with collimated fibres (43,69). As ceramic fibres are found to react with the matrices, various diffusion barrier

coatings were explored including ZrN, HfC, Al_2O_3 and W.

Silicon carbide fibres are available in several forms and are listed in Table-16. Polycrystalline silicon carbide fibres, produced by firing organic silicon based polymers at high temperature, have not been used as reinforcing agents in brittle-ductile composites intended for high temperature applications. Silicon carbide fibres with either tungsten or carbon cores have been used as reinforcing agents in brittle-ductile composites. Both types of SiC filaments have excellent elevated temperature properties, however filaments with carbon core are not only cheaper and have lower density but also have better 100 hours stress rupture properties at temperatures up to 1316 C. The 100 hour stress rupture values at 1093 C for SiC (carbon core), SiC (tungsten core) and the best metallic wire of $W - Re - Hf - C$ alloy are 1.93, 1.07 and 1.45 GPa respectively. The advantage of using SiC (carbon core) becomes more apparent when these stress rupture values are divided by their respective density values. The specific 100 hours stress rupture values at 1093 C are $5.86 \times 10^5 N.m.kg^{-1}$ for SiC (carbon core), $3.29 \times 10^5 N.m.kg^{-1}$ for SiC (tungsten core) and $0.765 \times 10^5 N.m.kg^{-1}$ for the strongest metallic alloy wire $W - Re - Hf - C$. Similar superiority is exhibited by SiC (C core) fibres over these materials at temperatures up to 1316 C (48). The room temperature properties of these fibres are listed in Table-16.

Carbon fibres have excellent room temperature properties and are listed in Table-16. They also have excellent high temperature (up to 2000 C) properties but only under inert conditions. At temperatures above 500 C, carbon fibres are known to oxidize rapidly in air. Thus, for their use as reinforcement in high temperature matrices, they should be protected completely from oxidation.

Potassium titanate fibre, having a chemical composition of $K_2O - 6TiO_2$, is a transparent and fibre-like or needle-like crystal. It has been recently developed and has good properties, which are also listed in Table-16.

Hot pressing of either fibres with powdered matrices or stacks of mono-layer tapes with binder has been commonly employed for the fabrication of brittle-ductile composites (42,43,48,69). Electroplating (44) and electroless nickel deposition (51) processes were also used to prepare these composites.

3.2.2 Fibre/Matrix Interaction and Properties

Although silicon carbide filaments have high oxidation resistance and excellent elevated temperature properties, they react with most metallic matrices at high temperatures. Therefore, in order for them to be used as reinforcement in high temperature matrices, they have to be protected with a diffusion barrier coating compatible with the selected matrix.

Cornie et al. (42) studied the effects of interface reactions on the properties HfC coated SiC (W core)/superalloy matrix composites. Based on the compatibility studies, HfC was reported to be an effective diffusion barrier to the inter-diffusion of nickel base superalloys (Waspalloy and Hastelloy X) and high strength SiC (W core) filaments for times greater than 200 hours at 1093 C. However, cobalt base matrix (Haynes 188) showed extensive interaction with HfC coating after 200 hours at 1093 C. The effect of coating thickness on the filament strength was also studied and

it was shown that, after a critical coating thickness of 2.4 μm, the strength of the SiC fibres starts to decrease, and with a coating thickness of about 5 μm the strength of the filament decreased from 3720 MPa to only 1741 MPa. The mechanical properties of SiC (W core)/Waspalloy composites showed a disappointingly small gain over the matrix properties and a maximum of 25% of the fibre strength was realized in the composites. The small gain in the properties of composites was attributed to misalignment of the fibres, chemical interaction between fibres and the matrix through coating defects and reduction of filament strength due to the presence of a brittle diffusion barrier.

Karpinos et al. (43) reported the use of alumina as a diffusion barrier coating on SiC (W core) filaments in a matrix of $80Ni - 20Cr$ alloy. It was concluded that alumina coating does inhibit mass transport between the fibres and the matrix and can be employed at temperatures not exceeding 1100 C for periods of the order of 50 hours. At higher temperatures and longer durations complex reactions occur, involving the formation of carbides and silicides of the metals present, resulting in total degeneration of SiC filaments.

Ahmed et al. (48) explored the use of tungsten as a diffusion barrier coating on SiC (C core) filament for their use in $FeCrAlY$ matrix. Tungsten was chosen as a diffusion barrier coating because, as demonstrated in Section 3.1, $W/FeCrAlY$ composites have been successfully fabricated without the requirement of any diffusion barrier coating and were shown to have adequate high temperature properties. Chemical vapor deposition was used to deposit up to 12.7 μm thick coating of tungsten on silicon carbide (C core) fibres. The tensile properties were degraded by the application of tungsten coating by about 35% at room temperature, about 25% at 1200 C and about 20% at 1600 C. SiC (C core)/$FeCrAlY$ composite panels were made by vacuum hot pressing of mono-layer tapes and contained about 30-33 volume percent fibres. Composite specimens showed UTS values up to 696 MPa at 1093 C, and limited stress rupture data indicate that the composite could withstand 244 MPa for more than 670 hours at 982 C. However, excessive fibre/coating interaction was reported in specimens exposed to 1093 C for longer periods of time. Further work on other diffusion barriers is on going (48).

Carbon fibre reinforced nickel matrix composites have been considered for some time as candidates for high temperature service. Unfortunately carbon fibres in such composites were found vulnerable to oxidation and structural degradation. Both processes can lead to complete loss of favourable mechanical properties of the fibre. Warren et al. (51) studied the high temperature compatibility of carbon fibres with nickel. Different types of carbon fibres, including rayon base and PAN base (HM and HT), were coated with nickel by a variety of methods (electroless, electrolytic, carbonyl and physical vapor deposition). It was reported that over 1 hour exposure in flowing argon atmosphere and at temperatures above 800 C, nickel coated carbon fibres undergo a transformation of structure to crystalline graphite with a consequent loss of strength and elastic modulus. Resistance to this recrystallization was found to be related to fibre type and the final graphitization temperature used in the fibre manufacture. Rayon base fibres, high modulus PAN base fibres and high strength PAN base fibres exhibited recrystallization temperatures (i.e temperature for 50% recrystallization in 1 hour) of 1250 C, 1200 C and 900 C respectvely. The recrystallization temperature was not affected by the type of nickel coating, but was considerably reduced in the presence of small quantities of air in the argon atmosphere for high modulus fibres. The high strength fibres were also degraded by air or hydrogen surface attacks at temperatures well below the recrystallization temperatures. It was however concluded, that for high temperature applications, the problem of recrystallization can be overcome by proper selection of the carbon

fibre type and the matrix alloy.

Zabolotskii et al. (44) studied reaction between carbon fibre and nickel in the presence of either ZrN or TiC coatings as diffusion barriers. It was concluded that ZrN coatings failed to prevent carbon fibre from reacting with nickel. However, TiC coatings were more effective in slowing the recrystallization process and the rate of dissolution of fibres in nickel, consequently the strength loss of carbon fibres was reduced.

Fukunaga et al. (69) reported the results of preliminary tests on new potassium titanate fibres in nickel matrix. One hour exposure at 850 C in air did not produce any interface reaction, however no higher temperature exposure results or mechanical characterization data on the composites were reported.

3.3 Ductile-Brittle Systems

As mentioned in Section 2.3, one way of tackling the problem of brittleness in ceramics is through the use of ductile wires as reinforcing agents. These wires may act as barriers to crack propagation and hence increase the work of fracture. Although considerable promise was shown by ductile-brittle composites (Section 2.3), it is surprising that only three papers have been identified in the open literature on these systems in the post 1975 period.

In Table-10, the current activities on ductile-brittle composites are listed. It can be seen that only two types of wires i.e Nb and Ta, are being examined presently as reinforcing agents in the matrices of silicon carbide, silicon nitride or molybdenum disilicide. The major limitation in these systems is that the metal reinforcing agent must remain solid during the high temperature pressing or sintering of the ceramic or glass matrix, and must retain its strength after the operation. These temperatures are generally in excess of 1450 C and therefore only refractory metal wires may be used. Brennen (102) reported that in silicon nitride matrix, refractory metal wires of Nb, W and Mo became very brittle after hot pressing at 1675 C. It was observed that upon impact, the crack would propagate right through the wire without any energy absorption by crack deflection. However, tantalum wires retained sufficient ductility even though a silicide reaction layer was formed at the interface. Hot pressing or cold compacting plus sintering of powdered matrices with pre-collimated fibres are the two fabrication methods used for producing ductile-brittle composites.

Brennen (102) reported increased impact strength of silicon nitride through the use of tantalum wire reinforcement. Tantalum wire reinforced, silicon nitride matrix composite containing about 25% wires was prepared by hot pressing at 1675 C for 30 minutes in argon. The matrix powder consisted of alpha silicon nitride and about 5% MgO. Composite made from 0.635 mm diameter tantalum wire showed Charpy impact strength of about 24 Joules up to about 700 C, after which it decreased gradually to 6.8 Joules at 1300 C. In contrast, unreinforced hot pressed $Si_3N_4 + 5\%MgO$ showed Charpy impact strength of approximately 0.68 Joules between room temperature and 1300 C. From room temperature to about 700 C, the composite specimens fractured in a combined mode comprising ductile wire elongation and interfacial splitting. Above 700 C the composite specimens failed mostly by ductile fibre fracture. As the interfacial splitting type fracture, which results in a large number of small pieces, is preferable from the practical standpoint, larger diameter

(1.27 mm) tantalum wires were also investigated. Even though the wire strength remains the same, more deformation and hence larger energy absorption could possibly occur with larger diameter wires, thus allowing the interfacial splitting process to take place before the wire deforms sufficiently to fracture. Indeed, the results of the Charpy tests on composite specimens with larger diameter tantalum wires showed no drop of Charpy impact strength up to 1300 C. In fact, the test at 1000 C essentially stopped a 20 ft-lb hammer, giving the highest impact strength of 30 Joules.

In the same study (102), instrumented Charpy tests were also performed and it was concluded that for Ta/Si_3N_4 composites a threshold energy level exists below which no damage occurs. This threshold energy level was found to be about 4 Joules for 25 vol.% - 0.635 mm dia. Ta/Si_3N_4, and was considerably higher than for un-reinforced silicon nitride. Furthermore, ballistic impact tests at room temperature and at 1300 C also showed that Ta/Si_3N_4 composites are far superior to un-reinforced silicon nitride.

Kaganawa et al. (106) studied the fracture behavior of SiC matrix composites reinforced with helical as well as straight tantalum wires. Helical tantalum wires were used to obtain good stress transfer, even if the wire/matrix interface is very weak, by deformation of the geometrical shape of the helix. Cold compacting plus vacuum sintering produced composites with about 60 % of the theoretical density of the matrix. The volume fraction of wires in the composite ranged from 1-4 volume percent. It was found that the fracture of composites reinforced with tantalum wires, whether straight or helical, was not as catastrophic as that of SiC matrix alone, due to bridging of the cracks and transference of load to the wires. The maximum load sustained by the specimens after the matrix fracture was larger in the helical wire composite than the straight wire composites. The total work of fracture was observed to depend on the geometry of the reinforcing wires and showed considerable improvement over the matrix material.

Fitzer and Remmele (101) studied niobium wire reinforced molybdenum disilicide matrix composites. Molybdenum disilicide is known as a high melting point inter-metallic with an exceptional oxidation resistance in air up to 1600 C. Composite specimens were produced by hot pressing and contained about 40 vol. percent niobium wire. Although the composites showed a decrease in Young's modulus as compared to the unreinforced molybdenum disilicide, the flexural strength increased two folds along with a considerable increase in the work of fracture.

3.4 Brittle-Brittle Systems

In the past twelve years, at least 31 papers have been published on composites in which both constituents are brittle by nature. These papers are summerized in Table-8. There appears to have been more work on brittle-brittle composites in the post-1975 period than on any other form of high temperature composite with the exception of ductile-ductile composites. Compare 31 publications against 3 for ductile-brittle systems and 6 for brittle-ductile systems. It can also be noted that the level of interest in brittle-brittle composites has increased considerably since 1975 (pre 1975 - 4 papers, post 1975 - 31 papers). Even so, brittle-brittle composites are not nearly in as advanced a state as are ductile-ductile composites. The increased interest in brittle-brittle composites can be attributed directly to the successful demonstration of the capabilities of carbon/carbon composites and carbon or silicon carbide fibre glass matrix composites. These

composites show that brittle matrices can indeed be reinforced by brittle fibres accompanied with an increase in toughness and other properties. Carbon-carbon composites are fairly well established (108,116) and as mentioned in Section 2.4, are finding use where extremely high temperature (> 2000 C) but short duration service is required. Due to their poor oxidation resistance, carbon-carbon composites are not considered for use in heat engine applications where extended high temperature exposure is required and hence will not be discussed in detail in this review.

3.4.1 Reinforcing Filaments

The reinforcing agents used for ceramic matrix composites are mainly silicon carbide fibres and whiskers (46,71,76,80-82,85,88,91,92,94,99,124,126). Carbon fibres were also explored to reinforce brittle matrices (39,108,109,111,112).

Silicon carbide fibres are available as either monofilament or yarn. Monofilament SiC fibres consist of a carbon or tungsten core on to which a thick layer of silicon carbide is deposited by chemical vapor deposition methods. Carbon core filaments are more suited for high temperature applications as tungsten in tungsten core filaments tends to react with SiC at high temperatures. Currently monofilament SiC fibres (C core) with a carbon doped surface are also available. The (free) carbon doped layer (about 1 μm thick) can act as a sacrificial layer and may be reacted extensively with the matrix without degrading the performance of the fibre. Silicon carbide yarn or tow, developed in Japan, consists of about 2000 fibres per tow with an average fibre diameter of about 10 μm. Both monofilament SiC fibre and SiC yarn are comprised of polycrystalline beta silicon carbide which, upon exposure to temperatures above 1250 C, undergo excessive grain growth resulting in the degradation of fibre properties.

Silicon carbide whiskers, on the other hand, are single crystals containing both beta and mixed alpha and beta phases of SiC. The average diameter of the whiskers is about 0.6 μm and a length of 10-80 μm. The whiskers are usually manufactured from rice hulls and possess very high strengths up to 7000 MPa. Silicon carbide whiskers have excellent thermal stability and can be exposed up to 1900 C without any degradation in properties.

Carbon fibres are also tried as reinforcing agents in ceramic matrices. The poor oxidation resistance of carbon fibres in air has restricted their use in systems which are designed either for low temperature applications or for high temperature applications with short time limited use. Currently, two dimensional carbon fibre cloth preforms are also being explored with various brittle matrices.

The properties of the currently available carbon and silicon carbide fibres are listed in Table-16.

3.4.2 Matrix Materials

Almost all structural ceramic materials have been explored as matrices (127). Silicon nitride (46,71,85,86,93,94,99,109,122,123),siliconcarbide (71,82,85,94,99,100,119,121,126),alumina (46,71,80,104,120) and various glasses and glass ceramics (76,81,88,91,92,103,105) have received the most attention for use as matrices with brittle fibres. Other matrix materials explored included mullite (46,71,120), boron carbide (46,100), silica (82), titanium carbide (100), boron nitride (100), zirconia (124) and hybrid materials such as C-SiC (39,100) and C-TiC (112).

Glasses such as borosilicate glass, aluminosilicate glass, high silica glass, and glass ceramics such as various types of lithium aluminosilicates and magnesium aluminosilicate have the maximum use temperature in the range of 600-1250 C. These materials can be incorporated as matrices with relative ease and are mainly being explored by the United Technologies Research Center and the Corning Research Labs. in the United States (126,128).

3.4.3 Fabrication Processes

The fabrication processes for brittle-brittle composites have recently been reviewed (126,127, 128). The fabrication processes can generally be divided into three major groups and are briefly described in the following sections:

3.4.3.1 Slurry Infiltration and Mixing Techniques

Slurry infiltration is probably the most common technique to produce brittle-brittle composites. With this technique the fibre or preform, for example a tow, is impregnated by passing it through a slurry containing the matrix material. The infiltrated tow is usually wound on a drum for collimation and is then dried. Dried and collimated single ply tapes are then cut to proper size and subsquently laid into a desired configuration for hot pressing.

The slurry mixture usually contains at least three components, the carrier liquid, the matrix powder and an organic binder. Wetting agents are also employed sometimes to facilitate infiltration. After burning out of the binder, hot pressing is performed to consolidate the matrix.

This technique has been used most effectively with glass and glass-ceramic matrix composites (76,81,88,91,104,122). These materials are typically hot pressed at temperatures near or above the softening point of the glass, such that densification readily occurs with viscous flow of the matrix. However, in refractory crystalline matrix systems, where even higher processing temperatures are required to densify the matrices, slurry processing has been less effective because of the absence of viscous flow. The major problems that arise are fibre degradation or damage resulting from mechanical contact with the refractory particles, fibre oxidation and other fibre-matrix chemical reactions and grain growth within the fibres. Guo et al. (109) have, however, alleviated some of these problems by using liquid-phase sintering additives in a Si_3N_4 matrix with reduced hot pressing temperatures. They achieved high strength values equivalent to those of hot pressed

Si_3N_4, along with high toughness values ($K_{1c} = 15.6MPa\sqrt{m}$) in carbon fibre reinforced material.

Simple mixing of chopped fibres or whiskers with ceramic powder or slurry followed by drying and hot pressing is another commonly used technique to produce isotropic composites (46,71,80,92,105,120,123,124). The major problems associated with this technique are the loss of isotropic behavior resulting from preferred fibre orientation induced by uniaxial pressing and whisker agglomeration. The degree of fibre orientation unfortunately increases for higher aspect ratio whiskers, which are desirable for strength and toughness. Hot isostatic pressing of vacuum capsulated material may alleviate this problem. Improvements in whisker dispersion methods should help in obtaining uniform whisker distribution in the composites.

3.4.3.2 Chemical Reaction Techniques

Chemical vapor deposition (CVD) has been used to produce coatings of tailored compositions on fibres. These coatings offer environmental protection for fibres and provide a broad range of tailored interface properties. Both oxide and non-oxide coatings can be easily deposited on a substrate. Recently an extension of this technique known as chemical vapor infiltration (CVI) has been explored considerably to form complete ceramic matrices around fibre preforms (85,86,93,94,99,100,112,119,125). The main disadvantage of this process is the slow deposition rates. By manipulating pressure and temperature gradients during deposition on a fibre preform contained in a die chamber with specially designed gas flow characteristics, Caputo et al. (94,99) achieved 70-90 % dense SiC and Si_3N_4 matrices on SiC and Si_3N_4 fibre preforms. Furthermore, these results were obtained in 2-12 hours at a gas pressure of 100 KPa, this is a remarkable improvement over previous CVI studies, during which it took several weeks to achieve the same density.

Other advantages of CVI process include the potential for forming complex three dimensional shapes, its ability to deposit a wide variety of material compositions including hybrid multiphase matrices, and its requirement of only a single step for infiltration. Deposition temperatures are still quite high, and interface reactions and fibre degradation due to high temperature exposure may pose some problems with certain fibre/matrix combinations.

In-situ reaction bonding techniques, such as those used to produce reaction bonded silicon nitride (RBSN) from silicon powder, can be easily modified to produce whisker composites. The whiskers can be dispersed into silicon powder before nitridization. Very high room temperature flexural strengths (900 MPa) are reported (as mentioned in Reference 128). This technique, although not very well studied, has the potential of being easily incorporated into the current practices of producing reaction bonded ceramics.

3.4.3.3 Sol-Gel and Polymer Pyrolysis Methods

Other methods of fabrication for ceramic matrix composites include sol-gel and polymer pyrolysis techniques. Although not widely used, they offer lower processing temperatures, com-

positional homogeneity, greater ease of infiltration with possible adaptation to existing ceramic fabrication techniques, and the potential of forming unique multi-phase matrices. The major disadvantages, however, include high shrinkage and low yields (96,128) compared to slurry techniques, and the necessity of having another processing step for densification. These processes are in the very early stages of development and hold considerable promise for the future.

3.4.4 Mechanical Properties

The following are the major factors contributing to strength and toughness of the brittle-brittle composites (84):

1. For optimum strength and stiffness continous fibres or discontinous whiskers of length greater than a certain critical length should be employed, and the difference in moduli and strengths of the matrix and reinforcement should be as large as possible. Fibres should be unidirectionally aligned parallel to the tensile axis to prevent the occurrence of shear deformation or bending moments which would reduce the effective tensile strength of fibres. Since the critical length of the fibre depends on the interfacial shear stress, a strong chemical or frictional bond is desirable.
2. For optimum toughness, fibre pullout is essential and aligned discontinous reinforcement with fibres of length equal to the critical length should ideally be employed. Weak interfaces are required to promote delamination and fibre pullout effects.

Thus for brittle-brittle composites, a compromise between strength and toughness is necessary. In cases where increasing the toughness of the ceramic matrices is the only requirement, weak interface bonding should be promoted. However, only frictional bonding between fibres and the matrix has also provided composites with increased strengths and toughness values in certain brittle-brittle composites.

In the following sections, the mechanical properties of brittle-brittle composites, classified on the basis of matrices alone are discussed seperately.

3.4.4.1 Glass and Glass-Ceramic Matrix Composites

The main advantage of using glasses and glass-ceramics as matrices is the fact that the viscosity of these materials can be greatly reduced at temperatures above their softening point. This feature allows the matrix to be readily deformed and to flow around the fibres during fabrication, thus providing dense composites without much porosity.

Earlier work on glass matrix composites was done with carbon fibres, and room temperature strength as high as 700 MPa was reported (126). Elevated temperature testing of carbon fibre/borosilicate glass composites showed that the strength loss is perceptible only above 500 C, due to the oxidation of carbon fibres. When compared to carbon fibre/epoxy matrix composites,

carbon fibre/glass matrix composites offer a wider range of operating temperature (up to 500 C). Further, the negative coefficient of thermal expansion (CTE) of carbon fibres can still be exploited to produce glass matrix composites with near zero CTE over a wider range of temperature. Carbon/glass composites are also characterized with a low coefficent of friction, high wear resistance and excellent toughness.

In an attempt to increase the high temperature capability of glass matrix composites, carbon fibres were replaced by more oxidation resistant silicon carbide based fibres [Table-16]. Work then progressed and higher melting point glasses and glass ceramics were exploited as matrices (76,81,88,91,92,103,105). In Table-17, some of these matrix materials are listed along with their maximum use temperatures.

Figure-10 shows the three point flexural strength in argon versus temperature for unidirectional silicon carbide yarn reinforced LAS I, LAS II and LAS III matrix composites. It can be seen that at 1000 C, the flexural strength shown by all three composites is higher than their respective room temperature strength. Further, SiC yarn/LAS III composite has flexural strength values of over 800 MPa at 1200 C, which compares very well to other monolithic ceramics at that temperature.

SiC yarn/LAS composites also have excellent fracture toughness. Unidirectionally reinforced composites have demonstrated fracture toughness values of about 17 $MPa\sqrt{m}$ at room temperature and increasing to about 25 $MPa\sqrt{m}$ at 1000 C, as compared to the fracture toughness value of monolithic silicon nitride of 4.5 $MPa\sqrt{m}$ at room temperature (88).

In comparison to monolithic silicon nitride in an un-notched condition the SiC/LAS composite material is almost five times as impact resistant in 0 degree configuration and slightly more impact resistant in 0/90 degree configuration. However, in a notched condition, the 0 degree composite material is over fifty times as impact resistant as silicon nitride, while 0/90 degree material is almost thirty times as impact resistant. Other properties including thermal shock resistance, elevated temperature creep and fatigue of SiC/LAS composite material also compare very favorably to monolithic silicon nitride material (88).

Elevated temperature properties of SiC/LAS composites are sensitive to the testing environment. Although not much work has been reported in this area, high temperature oxidative embrittlement problems need to be resolved for these composites before they can gain wide acceptance for elevated temperature applications.

Mono-filament silicon carbide fibres with carbon core and silicon carbide whiskers were also used to reinforce glass and glass ceramic matrices. Although mono-filament SiC/MAS composite material also showed considerable improvements in mechanical properties over monolithic MAS material, SiC yarn is favoured as a reinforcing agent due to the ease of composite fabrication. SiC whiskers/LAS III composite material showed no oxidative embrittlement effects, but it fractured in brittle fashion due to strong fibre/matrix bond and lack of a thin, carbon rich crack deflecting layer. Consequently, significant improvements in strength and toughness were not obtained in whisker reinforced composites (126).

3.4.4.2 Silicon Nitride Matrix Composites

Silicon nitride is of great interest for high temperature structural applications. Its use is limited by its relatively low fracture toughness and the fact that its mechanical properties begin to degrade at temperatures above 1200 C due to the glassy phase formed at the grain boundaries by the sintering aids normally employed for densification.

Most of the work reported in the open literature on silicon nitride matrix composites is focused primarily on the fabrication aspect (71,85,86,93,94,99,109,122,123), and very little data is available on the properties of these composites. Further, the properties reported are only room temperature properties. Although these composites are intended for high temperature applications, elevated temperature property characterization work is still lacking.

Guo et al. (109) and Guo (118) have reported that silicon nitride matrix can be reinforced by carbon fibres. Silicon nitride powder requires hot pressing temperatures in excess of 1700 C to acquire about 99% density. As carbon fibres react extensively with the matrix at this temperature, various sintering aids were investigated to lower the hot pressing temperature. It was found that additives from the $LiF - MgO - SiO_2$ system can lower the hot pressing temperature to about 1450 C. Carbon fibre reinforced silicon nitride matrix composites containing about 30 volume percent fibres were then prepared using this new additive. The properties of the composite and un-reinforced silicon nitride are listed in Table-18. Although a slight decrease in strength and modulus values of the composite was observed, the fracture toughness value increased significantly from about 3.7 $MPa\sqrt{m}$ for un-reinforced silicon nitride to about 15.6 $MPa\sqrt{m}$ for 30 vol.% C/Si_3N_4 composite. However, elevated temperature properties were not evaluated for the composite.

Bhatt (122) reported the room temperature mechanical and physical properties of silicon carbide (mono-filament) reinforced silicon nitride matrix composites containing 23 and 40 volume percent fibres. It was concluded that room temperature tensile and flexural strengths increased with volume fraction of fibres and were significantly higher than un-reinforced reaction bonded silicon nitride of comparable porosity [Table-19]. The fractured surfaces of the composite appeared to be fibrous, which is indicative of weak interfacial bonding and tougher material.

Shalek et al. (123) used silicon carbide whiskers to reinforce silicon nitride. Silicon carbide whisker content ranged from 10 to 40 volume percent, and three hot pressing temperatures viz. 1600 C, 1750 C and 1850 C, were investigated. It was shown that increasing the whisker volume percent slowly decreases the fracture stress. Composites prepared by using higher hot pressing temperatures showed higher strength levels presumably due to the conversion of equiaxed alpha-silicon nitride to beta-silicon nitride, which is more fibrous in structure. Fracture toughness values, however, increased with increasing whisker volume percent. For specimens hot pressed at 1750 C the fracture toughness values increased from about 7 $MPa\sqrt{m}$ for 0 volume percent whisker content to 10-12.5 $MPa\sqrt{m}$ for composites containing 10-30 volume percent whiskers. Fractured surfaces of the specimens showed very little fibre pull-out effect, indicating a strong interfacial bond. It was suggested that crack deflection and/or matrix microcracking were the main toughening mechanisms in operation. However, further improvement in toughness can potentially be realized by incorporating a weaker interface bond. Work in this direction is still needed.

3.4.4.3 Silicon Carbide Matrix Composites

As with silicon nitride matrix composites, most of the work reported in the open literature on silicon carbide matrix composites deals with the fabrication aspect of these composites (85,94,99,100,119, 125). Mechanical property data of only a preliminary nature has been reported so far (99,119,121,125), and most of it is room temperature flexural strength data.

Caputo and co-workers (99,119,125) investigated the use of a chemical vapor infiltration (CVI) technique to prepare SiC/SiC composites. Silicon carbide in the form of fibres, chopped fibres and cloth, of either satin or plain weave, was used as reinforcing agent in a CVI-SiC matrix. In Table-20, the properties of SiC matrix composites are summerized. It can be seen that even though the densities of the composites are low, unidirectionally reinforced composites show good flexural strength (>400 MPa). Two dimensional cloth reinforced composites show rather poor room temperature flexural strength probably due to the low densities obtained.

One study (121), reported the use of carbon fibres as reinforcing agents in silicon carbide matrix along with SiC/SiC composites. High bending strengths, greater than 300 MPa for SiC/SiC and higher than 500 MPa for C/SiC composites, are reported at all temperatures below 1300 C in an inert atmosphere. Excellent fracture toughness values were reported (> 25 $MPa\sqrt{m}$) for both types of composite. Further, it was shown that 500 hours exposure at 1100 C in an oxidative atmosphere did not degrade the strength of SiC/SiC composite.

These initial studies show that SiC matrix composites have good high temperature application potential, however, exhaustive high temperature characterization of these composites remains to be carried out.

3.4.4.4 Other Brittle Matrix Composites

Silicon carbide whiskers were used in matrices of alumina and mullite (46,71,80,120) to increase toughness. Typically 99% theoretical density was obtained by hot pressing of whisker/matrix mixtures. Becher et al. (71,120) noted that room temperature four point flexural strength of alumina matrix composites increased with increasing silicon carbide whisker content, and strength levels as high as 850 MPa were obtained with 40-60 volume percent whiskers. However, composites showed a slight decrease in strength with increasing temperature up to 1000 C, after which the decrease in strength was rapid. The room temperature fracture toughness value increased from about 4 $MPa\sqrt{m}$ for monolithic alumina to over 8 $MPa\sqrt{m}$ for composite containing 30 volume percent silicon carbide whiskers. The fracture toughness value of mullite matrix composite, containing 20 volume percent whiskers, was also shown to be twice that of the un-reinforced matrix. Chokshi and Porter (80) showed that SiC whisker/alumina composite is more creep resistant than un-reinforced alumina at 1500 C.

Bender et al. (124) showed that in zirconia matrix, silicon carbide fibres with a BN coating produces a stronger and tougher composite as compared to fibres without a coating. Fibres without a coating were shown to react chemically with the matrix at hot pressing temperature, while fibres with coating seem to alleviate this problem. Further, the coating also helped in creating a weaker

bond at the interface thus increasing toughness by the fibre pull out mechanism.

Composites with chemically vapor deposited hybrid matrices such as *C-SiC* and *C-TiC* (39,112) are also being studied. These composites are also showing good high temperature potential, but are in the very early stages of development.

4.0 SUMMARY AND CONCLUSIONS

For increased efficiency in heat engines, both automotive and aerospace industries are demanding materials capable of withstanding higher temperatures along with increased load carrying capacity and fracture toughness. In the un-reinforced state, superalloys appear to have reached their maximum potential for high temperature capability, with maximum use temperature around 1000 C. Monolithic ceramics can withstand higher temperatures, but their low fracture toughness has hindered their use. For further improvements, fibre or whisker reinforcement of these high temperature materials appear very promising. It has been shown that, with proper reinforcement, the use temperature of superalloys can be increased by at least 100 C and the fracture toughness of ceramics can be increased by a factor of 2-10.

This literature review should not be considered complete, since much work going on is proprietary in nature, and hence is not being referenced in the usual sources. Further, due to the export control regulations in the United States, much of the information on this subject originating in the United States is restricted. However, in this review, an attempt has been made to present the available information in some order and to point out the outstanding problems and areas which require further research and development.

4.1 Ductile-Ductile Composites

Metal matrix composites, reinforced with refractory metal fibres, are in the most advanced state of development among other high temperature composite materials. Tungsten or tungsten alloy wire has remained a major reinforcing agent, as wires of other refractory metals such as niobium, tantalum and molybdenum have shown severe compatibility problems with superalloy matrices. Commercially available lamp grade tungsten 218 or thoria dispersed tungsten wires are the most commonly used. Wires of tungsten alloy of the type $W - Hf - C$ and $W - Hf - Re - C$ have shown considerable improvement in high temperature properties over other tungsten base alloy wires [Figure-4]. However, the composition and thermo-mechanical processing of these alloys have not yet been optimized, and hence further improvement in properties is still possible.

The following are the important factors to be considered for proper selection of matrix materials:

1. Compatibility with fibres.

2. Oxidation resistance at elevated temperatures.

3. Diffusion bondability.

A number of nickel base superalloys and modifications of cobalt base superalloys have been investigated as matrices. Both types of superalloys have shown high temperature compatibility problems with tungsten base reinforcing wires. Iron base alloys of the type *FeCrAlY* have received considerable attention and at present appear to be the most promising candidates for use as matrix material. *FeCrAlY* has excellent high temperature oxidation resistance and hence, can be used without a protective coating in an engine environment. It is relatively soft and therefore can be easily used as matrix material, has high melting point and appears to be more compatible with tungsten wires, thus potentially eliminating the need for diffusion barrier coatings on the reinforcing filaments.

Solid state diffusion bonding has been the major composite fabrication technique. Prototype turbine blades have already been fabricated utilizing this technique [Figure-5]. Other techniques, such as vacuum investment casting and powder metallurgy processes, used to produce near net shapes also look promising. Solid state fabrication processes are favored as the interfacial reactions are better controlled at lower processing temperatures.

Fibre/matrix interaction has remained a major concern in ductile-ductile composites. Different types of interfacial reactions occur between tungsten fibres and nickel, cobalt or iron base superalloy matrices. These reactions include formation of solid solution zones, inter-metallic compounds and diffusion triggered recrystallization of heavily cold worked tungsten wires. Besides modification of the alloy composition, application of diffusion barrier coatings on the reinforcing fibres has also been investigated to alleviate interfacial reactions. It is well demonstrated in the literature that, with proper diffusion barrier coatings, these deleterious interfacial reactions can be restricted to a great extent. However, a thorough evaluation of various coatings in terms of their thickness, process of application, and their effect on the properties of the composite is still required.

The tensile and stress rupture properties are listed in Tables-14 and 15 respectively. Even though the mechanical property data is not complete, it can be seen that TFRS offer certain properties that are superior to those of the best superalloys in an un-reinforced state. Just on the basis of 100 hour creep rupture properties alone, TFRS offer at least 100 C advantantage in use temperature over the best un-reinforced superalloy. But when other properties of TFRS such as tensile strength, creep and fatigue resistance, and thermal conductivity are taken into account, they look even more attractive for replacing superalloys in high temperature applications. However, further research is needed to generate a complete data base for TFRS in order to properly design engine components and to take full advantage of the property improvents offered by TFRS over un-reinforced superalloys.

4.2 Brittle-Ductile Composites

There has not been much activity on brittle-ductile composites during the past decade. Only 6 papers [Table-9] were identified dealing with composites having brittle fibres in ductile

matrices. The primary reason for this low level of activity is excessive fibre/matrix interactions at elevated temperatures, and the lack of an effective diffusion barrier coating to prevent this interaction.

Silicon carbide, carbon and potasium titanate fibres have all been investigated in matrices of nickel, nickel base superalloys and $FeCrAlY$. Zirconium nitride, hafnium carbide, aluminium oxide and tungsten were tried as diffusion barrier coatings with varying degrees of success. Although brittle fibres offer better properties than ductile (metallic) wires as such, the development of brittle-ductile composites depend upon finding an effective diffusion barrier coating.

4.3 Ductile-Brittle Composites

The main reason for reinforcing brittle matrices is to improve their fracture toughness. Thus, relatively ductile, refractory metal wires look very promising as reinforcing agents in ceramic matrices. However, it is surprising to note that during the past decade only three papers [Table-10] have appeared in the open literature on composites belonging to this class.

The major problem appears to be the high temperatures required to hot press ceramic matrices. Wires of tungsten, niobium and molybdenum were found to be embrittled when hot pressed with silicon nitride matrix. Only tantalum wire was found to retain sufficient ductility and the fabricated tantalum/silicon nitride composite showed excellent results. Impact strength was shown to increase from 0.68 Joules for un-reinforced silicon nitride to 30 Joules for tantalum wire reinforced silicon nitride matrix composite. The mode of fracture was also changed, from catastrophic in unreinforced silicon nitride to a more forgiving interfacial splitting along with ductile fibre elongation type failure in Ta/Si_3N_4 composite. Reinforcement of silicon carbide matrix with tantalum wire also showed improved fracture toughness.

Tantalum wire reinforcement has great potential for improving the fracture toughness of ceramics without appreciable loss in strength. However, as illustrated in this review, very little work has been done so far on these composites. A considerable amount of work is needed in all phases including: fabrication techniques, matrix modification for optimum properties, composite characterization (both room and high temperature) and process optimization before tantalum reinforced ceramics can gain wide acceptance.

Continous tantalum wires have been used so far to fabricate uni-directional composites. Composites with chopped tantalum wire in a ceramic matrix to attain isotropic properties have not been investigated. As mentioned in this review, a considerable amount of work is being done to reinforce ceramic matrices by silicon carbide whiskers, which are also brittle in nature, in order to improve their fracture toughness. One of the major recognized mechanisms to improve fracture toughness in these systems is through the whisker pull-out. In brittle-brittle composites, the whisker pull-out mechanism requires weak interfacial bonding with a resultant strength penalty. However, if a ductile short fibre, such as chopped tantalum wire, is introduced in a ceramic matrix, there may not be any need for having a weak interfacial bond. Instead of whisker pull-out, ductile short fibres can plastically deform and fracture under load. Thus the energy will be absorbed in the ductile failure of the short fibres rather than in pull-out and, hence, fracture toughness might be

improved without any strength penalty.

4.4 Brittle-Brittle Composites

Brittle-brittle composites have attracted a high level of interest during the past decade, due to the superior properties demonstrated by carbon-carbon and silicon carbide - glass composites. Silicon carbide fibres of various types and whiskers have been the main reinforcing agents. Carbon fibres were also tried to reinforce ceramic matrices, but their low oxidation resistance has hindered their use.

Almost all structural ceramics, including silicon nitride, silicon carbide, alumina, mullite, zirconia, glasses and glass ceramics have been investigated as matrices. Glass and glass ceramic matrix composites with silicon carbide fibre reinforcement are relatively more established. Most of the work on silicon carbide and silicon nitride matrix composites has concentrated on their fabrication aspect and little property data is available.

In Table-21, the room temperature strength and toughness properties of some major ceramics and respective ceramic matrix composites are listed. It can be seen that in all the cases listed, strength and fracture toughness values are increased considerably through fibre or whisker reinforcement. Fracture toughness values as high as 56 $MPa\sqrt{m}$ have been reported for a SiC whisker reinforced Si_3N_4 matrix composite along with a flexural strength value of 800 MPa.

To summarize, brittle fibre reinforcement of ceramic matrices offers composite materials with excellent fracture toughness and strength properties. However, there is a need to improve the understanding of composite mechanical and physical properties and their relationship to fibre, matrix, diffusion barrier coating and interface characteristics. Further, high temperature and environmental effects on composites must be fully explored, as these composites are primarily intended for high temperature applications. Eventually comprehensive data bases will be needed for design, as well as to develop and verify structural analysis and failure models to optimize and maximize performance advantage in the more promising of these material systems.

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TABLE - 1
Materials suitable for high temperature use.

MATERIALS	RANGE OF MELTING POINTS C	PROBABLE RANGE OF USE TEMPERATURES C
Stainless steels	1371 - 1538	538 - 816
Nickel	1453	538 - 1316
Cobalt	1495	538 - 1316
Iron	1537	427 - 1204
Super alloys	1204 - 1427	649 - 1200
Refractory metals	1875 - 3410	982 - 2204
Ceramics	1316 - 3870	816 - 1649
Precious metals	961 - 1769	538 - 1538

TABLE - 2
List of materials most critical to the United States in 1983
by the Metals Properties Council.

MOST CRITICAL	MIDDLE	LEAST CRITICAL
Tantalum	Vanadium	Aluminium
Chromium	Rhenium	Copper
Platinum	Titanium	Molybdenum
Columbium	Tungsten	Magnesium
Manganese	Silver	Iron
Cobalt	Nickel	-
-	Gold	-

TABLE - 3
Research activities on ductile fibre reinforced ductile matrix composites prior to 1975.

FIBRES	VOL.%	MATRIX	FABRICATION METHOD	REFERENCE, ACTIVITY CENTER, YEAR
W		Cu,Co,L605, $Ni-Cr$,SS	Hot Press or Cold Press plus Sinter	4, NASA (USA), 1966
Mo - TZM $W-1\%ThO_2$ $W-3\%Re$ W		Ni base alloys	Slip casting plus Sintering	5, NASA (USA), 1968 (Review)
W		NimoCast 75 PE 10, EPD16 NimoCast 258	Vacuum Liquid Infiltration	6, NGTE (UK), 1965
Mo-TZM W	27-37 27-37	Hastelloy X 713C	Powder Metallurgy Techniques	7, USA, 1967
W		Nickel	Electro-plating or Vapour-plating	8, Univ. of Penn. (USA), 1968
$W-5Re$ $W-5Re$ W	20 20 20	IN 100 713 C 713 C	Vacuum Casting Vacuum Casting Vacuum Casting	9, NGTE (UK), 1970 (Review)
W $W-5Re$ Mo-TZM Nb-SU16 Nb-SU31 Mo-TZC	20 20 20 20 20 20	713 C 713 C Nimonic 75 115 and Nickel alloys	Vacuum Casting or Extrusion Vacuum Casting	10, NGTE (UK), 1970
W with Al_2O_3 coating	30-40	$80Ni-20Cr$	Vacuum Liquid Infiltration	11, (USSR), 1971
$W-Re-Hf-C$ $W-Re-Hf-C$ with coating	26-34 18-27	Ni alloy IN 100	Slip Casting Hot Pressing	12, NASA (USA),1972 (Review)
W		$Ni-Cr-W$ alloy	Dynamic Hot Press (Powder Matrix)	13, (USSR), 1973
W		Ni-base Superalloys	Slip Cast plus HIP or Mono Tape plus Hot Pressing	16, NASA (USA),1974

Table - 3 continued on the next page

TABLE - 3 continued

FIBRES	VOL.%	MATRIX	FABRICATION METHOD	REFERENCE, ACTIVITY CENTER, YEAR
W	23	*Ni*	Hot Powder Forging	17, Univ. of Chalmers (Sweden), 1974
W		*Ni*	Electroplating	18, Kyoto Univ. (Japan), 1975
Mo and *W*		*Ni*	Hot Forging	19, (USSR), 1975
W, *Mo*-TZM *W* – 5*Re*, *Mo*-TZC, *Nb*-SU16		*Ni* alloy	Vacuum Casting	22, NGTE (UK), 1970
W		*W* – *Fe* – *Ni* alloy	Cold Compaction of Powder plus Sinter	23, Univ. of Calif. (USA), 1973
W alloy *Mo* alloy		80*Ni* – 20*Cr* 80*Ni* – 20*Cr*	Hot Pressing of Powders	24, (USSR), 1974
W	22	*Ni*	Powder Pressing + Sinter + Forging	25, (Norway), 1973
Mo (discontinuous)		*Ni*	Co-extrusion of blended powder	26, AMMRC (USA),
W-218 CS *W* – 1%ThO_2 *W* – 5*Re* – 2ThO_3 *W* – 2ThO_2		56*Ni* – 25*W* – 15*Cr* – 2*Al* – 2*Ti*	Slip Casting + Sintering + HIPing	27, NASA, USA, 1970

TABLE - 4
Research activities on ceramic fibre reinforced metal matrix composites prior to 1975.

FIBRES	VOL.%	MATRIX	FABRICATION METHOD	REFERENCE, ACTIVITY CENTER, YEAR
SiC, Al_2O_3 ZrO_2, HfO_2 UO_2		Ni alloys W, Cb, Ta		5, NASA, USA, 1968 Review
Si_3N_4 SiC Alumina Saphire		Ni and Ni alloys Ni alloys Ni alloys	Hot Pressing Vacuum Casting	22, NGTE (UK), 1970
C (T50)	50	Ni	Electroless deposition + hot press	as in ref. 14
C (PAN-HM)	50	Ni	Electro-deposition + hot press	as in ref. 14

TABLE - 5
Research activities on ductile fibre reinforced brittle matrix composites prior to 1975.

FIBRES	VOL.%	MATRIX	FABRICATION METHOD	REFERENCE, ACTIVITY CENTER, YEAR
Ta		Si_3N_4	Hot Pressing	28, UARL (USA),1975
W		Si_3N_4	Hot Pressing	as mentioned in 28
Mo	6-12	Al_2O_3	Hot pressing	35,AECL,Canada,1971
Mo	10-20	ThO_2	Hot pressing	33, USA, 1960
Mo W with and without disilicide coating	20 20	Mullite Mullite	Vacuum hot pressing	34, GM, USA, 1966
W	20-30	SiO_2	Vacuum hot pressing	36, Sandia Labs, USA, 1972
Mo	5-20	Al_2O_3	Cold pressing plus sintering	as in ref. 84
Mo	20	Al_2O_3		"
Mo	10-20	HfO_2		"
W	10-25	Glass		"
Ni	5-50	Glass		"
Ni	2-12	Glass		"

TABLE - 6
Research activities on brittle fibre reinforced brittle matrix composites prior to 1975.

FIBRES	VOL.%	MATRIX	FABRICATION METHOD	REFERENCE, ACTIVITY CENTER, YEAR
Carbon	20-60	Pyrex glass Soda glass LAS glass Al_2O_3	Hot pressing of fibres with powdered matrices	29, UK, 1972
Carbon	20-60	Pyrex glass	Hot pressing of fibres with powdered matrices	31, UK, 1972
Carbon	20-60	Glass	Hot pressing of fibres with powdered matrices	32, UK, 1972
Carbon		Carbon		30, USA, 1974

TABLE - 7
Current research activities on ductile fibre reinforced ductile matrix composites.

FIBRES	VOL.%	MATRIX	DIFF. BARR.	FABRICATION METHOD	REF, ORIGIN, YEAR
W	50	*Ni*		Vacuum liquid infiltration	77,Denmark, 1975
W		*Fe* base powder alloys		Cold pressing plus Sinter forging	78, USSR, 1976
W		*Ni*		Liquid infiltration plus sinter forging	68,Denmark, 1976
$W - 1\%ThO_2$ $W - Hf - C$	45 30	*FeCrAlY* *NiCrAlY*		Solid state diffusion bonding of fibres+powder or matrix sheets	64, NASA, USA 1976
W $W - 1 - 2\%ThO_2$	20 20	Hastelloy X Haynes 188 *FeCrAlY* MAR M 200	*HfN* *HfN* *HfN* *HfN*	HIP'ing of monolayer powder tapes with fugitive binder	40, Westinghouse, Canada 1977
$W - 2\%ThO_2$	50-55	MAR M 200 Powder alloy		HIP'ing of monolayer powder tapes with sacrificial binder	61, Westinghouse, USA 1977
W		*Ni*		Electroplating	73, Westinghouse, USA 1977
$W - 2\%ThO_2$	40	MAR M 322 and its modifications		Vacuum investment casting	74, US Army, USA, 1977
$W - 1\%ThO_2$	30	*FeCrAlY*		Hot pressing	79, TRW, USA, 1977
W		*FeCrAlY*		Cost/benefit study	87, NASA, USA 1977
W		*FeCrAlY*		Cost/benefit study	89, NASA, USA 1977
W		*FeCrAlY*		Cost/benefit study	90, NASA, USA 1977
W		MAR M 200 Hastealoy X Haynes 188 *FeCrAlY*	*HfN* *HfN* *HfN* *HfN*	HIP'ing of fibres with powdered matrices	110, Westinghouse, Canada 1977

Table - 7 continued on the next page:

TABLE - 7 continued

FIBRES	Vol.%	MATRIX	DIFF. BARR.	FABRICATION METHOD	REF. ORIGIN, YEAR
$W - 1\%ThO_2$		*FeCrAlY* *Ni* base alloy		Hot pressing	75, NASA, USA 1978
$W - Hf - C$ $W - Re - Hf - C$ $W - ThO_2$ B-88 (*Co*) ASTAR (*Ta*)				High temperature wire fabrication study	45, NASA, USA 1979
$W - 2\%ThO_2$ $W - 1\%ThO_2$ $W - 3\%Re$	38-44	MAR M 322 standard and modified	*TaC*	Investment Casting	47, US Army, USA, 1979
W $W - Hf - C$		Inconel 600 Hastelloy X Nimonic 80A IN 102 *FeNiCrAlY* *FeCrAlY*		Hot pressing of monolayer tapes with sacrificial binder	50, NASA, USA 1979
$W - 1\%ThO_2$ W	50 65	*FeCrAlY* Ni base alloy		Hot pressing of stacked layers	53, NASA, USA 1979
$W - 1\%ThO_2$ $W - 2\%ThO_2$		MAR M 322E MAR M 200+Hf		Investment and continuous casting	56, TRW, USA 1979
$W - 1\%ThO_2$		*FeCrAlY*		Investment casting or diffusion bonding	57, NASA, USA 1979
$W - 1\%ThO_2$ TZM (*Mo*)	30-40 30-40	*FeCrAlY* *FeCrAlY*		Solid state diffusion bonding	58, TRW, USA 1979
$W - 1\%ThO_2$		*FeCrAlY*		Cold pressing plus sintering plus hot swaging	59, NSWC, USA, 1979
$W - 1\%ThO_2$		*FeCrAlY*		Cold pressing plus sintering plus hot swaging	62, NSWC, USA, 1979
$W - 2\%ThO_2$	21	304 stainless steel		Vacuum capsulation in matrix tubes plus HIP'ing	63, Chalmers Univ., Sweden 1979

Table - 7 continued on the next page:

TABLE - 7 continued

FIBRES	VOL.%	MATRIX	DIFF. BARR.	FABRICATION METHOD	REF., ORIGIN, YEAR
$W - 1\%ThO_2$		$FeCrAlY$		Hot pressing of monolayer tapes with sacrificial binder or powder.	65, NASA, USA 1979
W $W - 2\%ThO_2$	18-35 18-35	304 SS $Fe - 29Ni - 17Co$ (KOVAR)		Vacuum capsulation in matrix tubes plus HIP'ing	70, Chalmers Univ. Sweden 1979
$W - 2\%ThO_2$		304 SS		Vacuum capsulation in matrix tubes +HIP+hot swaging	72, Chalmers Univ. Sweden 1979
W		$FeCrAlY$		Diffusion bonding	66, USA, 1981
W $W - 1\%ThO_2$	45 45	AISI 1010 AISI 1095		Hot pressing	49, US Navy, USA, 1982
$W - 2\%ThO_2$	30	SS AISI 321 KOVAR Inconel 718 Hastelloy X		HIP'ing of bundles of fibres with powdered matrices	52, Chalmers Univ. Sweden, 1982
$W - 1.5\%ThO_2$	59	$FeCrAlY$		OVEREVIEW	60, NASA, USA 1982
W		Ni	ZrC ZrO_2 HfC HfO_2 TaC Al_4C_3 TiC	Hot pressing of fibres with thin compacted matrices	113, Japan, 1982
$W - 2\%ThO_2$		Ni		Electroplating	114, Sweden, 1982
W	6	Ni	TiC TiN	Cold pressing plus Sintering	116, Finland, 1982
W	50	Fe and Ni		Electroplating	117, Hungary, 1982
W	6-12	Ni	TaC TiN	Cold powder compaction +Sinter	55, Finland, 1983

Table - 7 continued on the next page:

TABLE - 7 continued:

FIBRES	VOL.%	MATRIX	DIFF. BARR.	FABRICATION METHOD	REF., ORIGIN, YEAR
$W - Re - Hf - C$		Waspaloy Incoloy 903 $FeCrAlY$ AISI 316		OVERVIEW	41, NASA, USA 1984
W	40	MAR M 200	HfN	HIP'ing	54, NRC, Canada, 1984
W	11-18	Nickel 316 L (SS)	ZrC ZrO_2 ZrN TaC TiC Al_2O_3 Cr_2O_3 Al_4C_3	Hot pressing of fibres with matrix in powder or foil form	107, Japan, 1985

DIFF. BARR. - Diffusion barrier coating.

TABLE - 8
Current research activities on brittle fibre reinforced brittle matrix composites.

FIBRES	VOL.%	MATRIX	DIFF. BARR.	FABRICATION METHOD	REF. ORIGIN, YEAR
Carbon		$C - SiC$		Carbon fibres densified with C then CVI with SiC	39, France, 1980
SiC fibres	35-65	Borosilicate glass		Hot pressing with powdered matrix	91, USA, 1980
SiC yarn	35-50	Borosilicate high silica glass		Slurry infiltration + vacuum hot pressing	76, USA, 1982
TiN particles		Si_3N_4		CVD	86, Japan, 1982
SiC fibres	50	LAS 1 glass		Slurry infiltration + vacuum hot pressing	88, USA, 1982
C,TiN,BN particles		Si_3N_4		CVD	93, Japan, 1982
Carbon	30	Si_3N_4		Slurry infiltration + hot pressing	109, China, 1982
Carbon		Carbon			111, Japan, 1982
Carbon 2D		$C - TiC$ hybrid		Chemical vapor Infiltration	112, France 1982
SiC whiskers	5-60	Al_2O_3, B_4C, mullite,Si_3N_4		Hot pressing of mixtures	46, USA, 1984
				REVIEW	83, USA, 1984
SiC fibres		SiC Si_3N_4		CVD	85, USA, 1984
SiC		SiC Si_3N_4		Chemical Vapor Infiltration	94, USA, 1984
				Polymer pyrolisis	96, NRL, USA, 1984

Table - 8 continued on the next page

Table - 8 continued

FIBRES	VOL.%	MATRIX	DIFF. BARR.	FABRICATION METHOD	REF., ORIGIN, YEAR
SiC whiskers		Al_2O_3, Si_3N_4 mullite, SiC		Hot pressing of mixture	71, USA, 1985
SiC whiskers		Al_2O_3		Hot Pressing	80, USA, 1985
SiC fibres		LAS II		Slurry infiltration + vacuum hot pressing	81, USA, 1985
SiC, Al_2O_3 graphite		SiO_2 SiC	BN	Diffusion barrier study	82, USA, 1985
SiC fibres	40	Mg alumino-Silicate and LAS glasses		Hot pressing	92, USA, 1985
SiC fibres		SiC and Si_3N_4		Chemical vapor Infiltration	99, USA, 1985
Carbon 2-D preforms		SiC, $SiC + C$, $SiCB_4C$, BN		Chemical Vapor Infiltration	100, France, 1985
SiC	50	LAS glass			103, USA,1985
SiC and FP alumina fibres		Alumina		Slurry infitration + cold pressing + Sintering	104, France, 1985
SiC	46	LAS II glass		Hot Pressing	105, USA,1985
Carbon		Carbon			108, Japan, 1985
SiC		SiC		CVD	119, USA,1985
SiC	<30 <30	Alumina Mullite		Hot Pressing	120, USA,1985
C, SiC		SiC			121, France, 1985
SiC	23-40	Si_3N_4		Slurry infiltration + Hot Pressing	122, USA,1985
SiC	10-40	Si_3N_4		Hot Pressing	123, USA,1986
SiC		Zirconia base	BN	Hot Pressing	124, USA,1986
SiC	22-45	SiC		CVD	126, USA,1986

DIFF. BARR. - Diffusion barrier coating

TABLE - 9
Current research activities on brittle fibre reinforced ductile matrix composites.

FIBRES	VOL.%	MATRIX	DIFF. BARR.	FABRICATION METHOD	REF., ORIGIN, YEAR
C		Ni	ZrN	Electroplating	44, USSR, 1976
SiC fibres	50 50 50	Waspalloy Hastelloy X Haynes 188	HfC HfC HfC	Diffusion bonding of monolayer tapes	42, AVCO, USA 1977
SiC fibres		$80Ni$-$20Cr$	Al_2O_3	Hot pressing of powder + fibres	43, USSR, 1977
C various grades		Ni		Electroless Nickel deposition	51, Chalmers Univ. Sweden, 1978
SiC		$FeCrAlY$	W	Vacuum hot pressing of monolayer tapes with binder	48, USA, 1979
Potassium Titanate fibres		Ni		Powder pressing	69, Japan, 1983

TABLE - 10
Current research activities on ductile fibre reinforced brittle matrix composites.

FIBRES	VOL.%	MATRIX	DIFF. BARR.	FABRICATION METHOD	REF., ORIGIN, YEAR
Nb	40	Molybdenum disilicide		Hot Pressing	101, West Germany, 1985
Ta	1-3	SiC		Cold pressing plus vacuum sintering	106, Japan, 1985
Ta	25	Si_3N_4		Hot Pressing	102, USA,1975

DIFF. BARR. - Diffusion barrier coating

TABLE - 11

Chemical composition of the alloys used as matrices in ductile - ductile composites during the past ten years. (nominal weight percent)

ALLOYS	*Ni*	*Co*	*Fe*	*Mo*	*W*	*Cr*	*Ta*	*C*	*Y*	*Ti*	*Zr*	*Al*	*Cb*	*Hf*
A) NICKEL BASE ALLOYS														
HASTEALOY X	50	2	18	9	-	21	-	-	-	-	-	-	-	-
INCONEL 713	Bal.	-	20	0.7	-	-	-	.1	-	-	-	-	-	-
NIMONIC 80A	Bal.	-	-	1.8	-	19.5	-	.1	-	2.4	.03	1.4	-	-
IN 102	Bal.	-	-	-	-	-	-	-	-	-	-	-	-	-
INCONEL 718	Bal.	-	20	3	-	18.0	5Nb	-	-	1	-	0.6	-	-
NiCrAlY	74.6	-	-	-	-	20.0	-	-	.4	-	-	5	-	-
MAR M 200+*Hf*	Bal.	10	-	-	12	9	-	.1	-	2.0	-	5	1	2
NICKEL ALLOY	Bal.	10	-	3	6	12	1.5	.3	-	3.0	-	4.6	-	-
NICKEL ALLOY	Bal.	-	-	-	25	15	-	-	-	2.0	-	2.0	-	-
B) COBALT BASE ALLOYS														
MAR M 322	-	Bal.	-	-	9	21.5	4.5	1	-	.75	1.5	-	-	-
MAR M 322 A	-	Bal.	-	-	20	21.5	4.5	1	-	.75	-	-	-	-
MAR M 322 B	-	Bal.	-	-	25	21.5	4.5	1	-	.75	-	-	-	-
MAR M 322 C	10	Bal.	-	-	25	21.5	4.5	.7	-	.75	-	-	-	-
MAR M 322 D	10	Bal.	-	-	25	21.5	4.5	.7	-	.75	-	-	-	-
MAR M 322 E	10	Bal.	-	-	25	21.5	3.5	.3	-	.75	-	-	-	-
MAR M 302	-	Bal.	-	-	10	21.5	9	.8	-	-	0.2	-	-	-
C) IRON BASE ALLOYS														
FeCrAlY	-	-	Bal.	-	-	23	-	-	1	-	-	5	-	-
KOVAR	29	17	54	-	-	-	-	-	-	-	-	-	-	-
316 L (SS)	12.9	-	Bal.	2.2	-	17.1	-	-	-	-	-	-	-	-
321(SS)	10	-	Bal.	-	-	18	-	-	-	0.3	-	-	-	-

TABLE - 12
Material characteristics important in turbine blade applications (60).

PROPERTY	SIGNIFICANCE TO DESIGN
CREEP AND RUPTURE	Limit allowable aerofoil metal temperature and stress.
HIGH CYCLE FATIGUE	Vibration stresses at all locations on the blade must be less than the endurance limit of the material as determined in smooth and notched bar tests.
LOW CYCLE FATIGUE	Determines design life, smooth bar data important to aerofoil leading and trailing edges, notched bar data important to dove tail and bleed holes in air cooled blades.
TENSILE PROPERTIES	Limits dovetail/shank design.
SHEAR AND TORSION	Adequate in conventional superalloys, but could be limiting in anisotropic materials, particularly in the dovetail area.
DENSITY	Affects blade and disk stresses
THERMAL EXPANSION	Affects blade expansion, important to gas leakage and tip rub.
INCIPENT MELTING	Affects over-temperature capability of aerofoil in the event of hot spots.
ELASTIC CONSTANTS	Affects blade material natural frequencies and thermal stresses.

TABLE - 13
Minimum property data needed to design turbine blades for developmental engines.

PROPERTY	TEMPERATURE RANGE C						
	RT	500	620	750	870	1000	1130
0.2% YIELD STRENGTH	x	x	x	x	x	x	x
ULTIMATE TENSILE STRENGTH	x	x	x	x	x	x	x
PERCENT ELONGATION	x	x	x	x	x	x	x
REDUCTION OF AREA	x	x	x	x	x	x	x
100 HOURS STRESS RUPTURE				x	x	x	x
1000 HOURS STRESS RUPTURE				x	x	x	x
0.2% PLASTIC CREEP				x	x	x	x
LOW CYCLE FATIGUE			x		x	x	x
HIGH CYCLE FATIGUE			x		x	x	
STABILITY - RT AND 900 C TENSILE DUCTILITY, CHARPY AND BALLISTIC IMPACT BEFORE AND AFTER 100 HOUR EXPOSURE TO CRITICAL ELEVATED TEMPERATURE.	x				x		
LOWEST MELTING TEMP.							
DENSITY	x						
THERMAL EXPANSION		x	x	x	x	x	x
THERMAL CONDUCTIVITY		x	x	x	x	x	x
SPECIFIC HEAT	x						
POISSONS RATIO	x						
MODULUS OF ELASTICITY	x	x	x	x	x	x	x

TABLE - 14

Experimentally measured tensile properties of tungsten fibre reinforced superalloy matrix composites reported since 1975.

REf	FILA-MENT	MATRIX	VOL%	DF BR	FIL. ORI. DEG.	TEST TEMP C	.2% YS *MPa*	UTS *MPa*	MD EL *GPa*	%EL	RA %
A. NICKEL BASE MATRICES.											
55	*W*	*Ni*	40-44	-	0	650	193	270	-	-	-
.			"	-	0	930	70	127	-	-	-
.			"	*TiC*	0	650	-	232	-	-	-
.			"	*TiC*	0	930	-	117	-	-	-
.			"	*TiN*	0	650	121	201	-	-	-
.			"	TiN	0	930	60	99	-	-	-
61	$W - 2\%ThO_2$	MAR M200	50-55	-	0	870	-	1157	-	1.67	-
Composites hot isostatically pressed at 1120 C, 138 *MPa* for 2 hours.			"	-	0	980	-	839	-	8.6	-
			"	-	10	980	-	638	-	2.6	-
			"	-	45	980	-	440	-	>12.4	-
			"	-	90	980	-	449	-	9.0	-
.			"	-	0	1090	-	595	-	24.5	-
.			"	-	10	1090	-	430	-	24.8	-
.			"	-	45	1090	-	147	-	29.7	-
.			"	-	90	1090	-	119	-	29.4	-
MAR M 200 only			-	-	-	870	-	840	-	-	-
"			-	-	-	980	-	523	-	-	-
"			-	-	-	1090	-	213	-	-	-
HSTW wire only			-	-	-	870	-	1371	-	-	-
"			-	-	-	980	-	1212	-	-	-
"			-	-	-	1090	-	1109	-	-	-
B. COBALT BASE MATRICES											
47 and 74	$W - 2\%ThO_2$	MARM322C	33	-	0	RT	-	345	-	0.2	-
		"	35	-	0	900	-	590	-	4.9	-
		MARM322D	43	-	0	980	537	545	-	4.7	-
.		"	44	-	0	1093	488	520	-	3.2	-
.		"	40	-	0	1150	392	420	-	4.0	-
.		"	44	-	0	1315	96	103	-	-	-
.		MARM322E	40	-	0	980	537	545	-	-	-
.		"	38	-	0	1093	419	434	-	-	-
.		"	40	-	0	1150	392	448	-	-	-

Table - 14 continued on the next page.

TABLE - 14 continued.

REF	FILAMENT	MATRIX	VOL.%	DF BR	FIL. ORI. DEG.	TEST TEMP C	.2% YS *MPa*	UTS *MPa*	MD EL *GPa*	%EL	RA %
	MAR M 322 C only		-	-	-	RT	710	-	-	0.5	-
	"		-	-	-	1093	214	214	-	3.6	-
	MAR M 322 E only		-	-	-	RT	303	448	-	9.0	-
	"		-	-	-	900	276	386	-	18	-
	"		-	-	-	980	110	117	-	-	-
	$W - 2\%ThO_2$ only		-	-	-	RT	-	2170	-	-	6
	"		-	-	-	650	-	1791	-	-	30
	"		-	-	-	870	-	1780	-	-	28
	"		-	-	-	1093	-	1309	-	-	25
	C. IRON BASE MATRICES										
45	$W - 1\%ThO_2$	AISI1095	-	-	0	RT	-	400	297	-	-
	AFTER HEAT TREATING		-	-	0	RT	-	938	293	-	-
70	$W - 2\%ThO_2$	304 SS	20	-	0	RT	-	650	-	-	-
	.		20	-	0	380	-	566	-	-	-
	.		20	-	0	600	-	470	-	-	-
	Composites hot		20	-	0	700	-	470	-	-	-
	isostatically pressed		20	-	0	980	-	300	-	-	-
	at 1050-1200 C and		25	-	0	RT	-	540	-	-	-
	150-250 *MPa*		25	-	0	200	-	700	-	-	-
	.		25	-	0	360	-	625	-	-	-
	.		25	-	0	500	-	560	-	-	-
	.		35	-	0	RT	-	660	-	-	-
	.		35	-	0	200	-	840	-	-	-
	.		35	-	0	360	-	710	-	-	-
	.		35	-	0	500	-	760	-	-	-
	.		35	-	0	700	-	600	-	-	-
	.		35	-	0	980	-	470	-	-	-
	$W - 2\%ThO_2$	KOVAR	25	-	0	RT	-	900	-	-	-
			25	-	0	600	-	500	-	-	-
58	$W - 1\%ThO_2$	*FeCrAlY*	35	-	0	RT	-	620	179	-	-
	.		35	-	15	648	-	746	-	19	-
	.		35	-	45	648	-	551	-	29	-
	Composites prepared		35	-	90	648	-	185	-	3.4	-
	by hot pressing		35	-	15	760	-	552	-	13	-
	.		35	-	45	760	-	169	-	24	-

Table - 14 continued on the next page.

TABLE - 14 continued.

REF	FILA-MENT	MATRIX	VOL.%	DF BR	FIL. ORI. DEG.	TEST TEMP C	.2% YS *MPa*	UTS *MPa*	MD EL *GPa*	%EL	RA %
.			35	-	90	760	-	111	-	6.5	-
As fabricated			35	-	0	RT	-	654	179	-	-
After creep testing at:											
1037 C for 1077 hours			35	-	0	648	-	737	-	3	-
1093 C for 990 hours			35	-	0	648	-	768	-	2.9	-
50	*W – Hf – C*	*FeCrAlY*	30	-	0	982	-	460	-	0.6	-
.			30	-	0	1093	-	381	-	0.3	-
Composites prepared			50	-	0	982	615	684	152	3.2	-
by hot pressing			<38	-	0	982	665	724	151	2.4	-
.			42	-	0	1093	428	>548	265	>1.6	-
.			44	-	0	1093	540	607	-	3	-

REF - REFERENCE
DF BR - DIFFUSION BARRIER COATING
FIL.ORI. - FILAMENT ORIENTATION
TEST.TEMP. - TEST TEMPERATURE
.2% YS - 0.2 % YIELD STRENGTH
UTS - ULTIMATE TENSILE STRENGTH
MD EL - TENSILE MODULUS OF ELASTICITY
RA - REDUCTION OF AREA

TABLE - 15

Stress rupture properties of TFRS reported since 1975.

REF	FILAMENT	VOL%	MATRIX	STRESS *MPa*	TIME TO RUPTURE Hours	TEMP. C	SP.ST N.m.kg^{-1} $\times 10^4$	LM PAR P
47	$W - 2\%ThO_2$	42	MAR M 322E	206	100	1093	1.57	30
74	$W - 2\%ThO_2$	43	MAR M 322E	228	103.2	1093	1.72	30.07
	"	45	"	172	239.4	1093	1.28	30.56
	-	-	"	48	89.3	1093	0.58	29.9
40	W	31	MAR M 200	130	100	1093	1.09	30
	-	-	MAR M 200	50	100	1093	0.42	30
50	W	35	INCONEL625	160	20.65	1093	1.30	29.1
	"	"	"	160	20.85	"	1.30	29.1
	"	"	"	190	4.6	"	1.54	28.2
	"	"	"	190	0.25	"	1.54	26.5
	"	"	"	134	3.99	1182	1.08	29.9
	"	"	"	134	6.69	1093	1.08	28.4
	"	50	"	280	6.59	"	2.01	28.4
	"	"	"	280	3.92	"	2.01	28.1
	"	"	"	210	29.39	"	1.50	29.3
	"	"	"	170	6.14	1182	1.22	30.2
	"	"	"	210	17.13	1093	1.50	29.0
	"	"	"	170	101.20	"	1.22	30.05
	"	"	"	170	93.04	"	1.22	30.0
	"	"	INCONEL600	270	3.49	"	1.95	28.0
	"	"	"	275	4.96	"	1.99	28.2
	"	"	"	212	25.79	"	1.53	29.2
	"	"	"	171	50.90	"	1.23	29.6
	"	"	"	168	13.62	"	1.21	28.8
	"	35	"	191	7.06	"	1.56	28.4
	"	"	"	174	6.91	"	1.42	28.4
	"	"	"	210	2.39	"	1.72	27.8
	"	"	"	132	27.04	"	1.08	29.2
	"	"	"	129	19.72	"	1.06	29.0
	"	50	*FeCrAlY*	280	0.19	"	2.07	26.3
	"	"	"	280	0.14	"	2.07	26.1
	"	"	"	240	1.62	"	1.77	27.6
	"	"	"	240	1.10	"	1.77	27.3
	"	"	"	210	5.55	"	1.55	28.3
	"	"	"	210	9.92	1182	1.55	30.5
	"	"	"	170	8.82	"	1.25	30.4

Table - 15 continued on the next page.

TABLE - 15 continued

REF	FILAMENT	VOL %	MATRIX	STRESS MPa	TIME TO RUPTURE Hours	TEMP. C	SP.ST $N.m.kg^{-1} \times 10^4$	LM PAR P
	〃	〃	〃	120	35.14	〃	0.88	31.3
	〃	〃	〃	120	32.20	〃	0.88	31.2
50	〃	35	〃	210	0.02	1093	1.78	24.9
	〃	〃	〃	170	22.50	〃	1.44	29.1
	〃	〃	〃	134	22.77	〃	1.13	29.1
	〃	〃	〃	110	49.15	〃	0.93	29.6
	$W - Hf - C$	〃	〃	397	1.79	〃	3.37	27.6
	〃	〃	〃	364	2.30	〃	3.09	27.8
	〃	〃	〃	287	9.09	〃	2.4	28.6
	〃	〃	〃	294	31.51	〃	2.5	29.3
	〃	〃	〃	209	213.87	〃	1.7	30.5
58	$W - 1\%ThO_2$	35	$FeCrAlY$	241	100.00	1093	2.07	30.0
	〃	45	〃	344	100.00	1093	2.71	30.0
64	W	41	$NiCrAlY$	220	0.6	1093	1.72	27.0
	〃	50	〃	220	1.2	〃	1.60	27.4
	〃	42	〃	207	21.3	〃	1.61	29.1
	〃	38	〃	158	115.6+	〃	1.21	30.1
	〃	〃	〃	172	126.6+	〃	1.38	30.1
	〃	〃	〃	196	65.3	〃	1.57	29.7
	$W - Hf - C$	35	〃	413	13.1	〃	3.4	28.8
	〃	31	〃	413	31.3	〃	3.5	29.3
	〃	35	〃	344	139.6	〃	2.8	30.2
	〃	28	〃	324	166.1	〃	2.7	30.3
	〃	35	〃	344	82.1	〃	2.8	29.9

SP.ST - Specific rupture strength (rupture strength/density)

P = $T \times 10^3(20 + \log t)$

where P - Larson - Miller Parameter

T - Temperature K

t - Rupture time in hours.

TABLE - 16
Properties of the ceramic fibres used in brittle-ductile composites.

FIBRE	PRECURSOR	TENSILE STRENGTH GPa	TENSILE MODULUS GPa	DENSITY g/cm^3
Silicon carbide	W core	3.1	420	3.15
	C core	3.45	400	3.0
	Yarn	2.7	200	2.55
	Whiskers	7.0	700	
Carbon	PAN	1.7-3.2	170-517	-0.5
	Rayon	0.6-3.2	41-525	to
	Pitch	1.1-2.1	379-689	-1.3
Potassium titanate $K_2O - 6TiO_2$	-	6.86	274	3.58

TABLE - 17
Glasses and glass ceramics suitable for matrices (126).

MATRIX TYPE	MAJOR CONSTITUENT	MINOR CONSTITUENT	MAXIMUM USE TEMPERATURE
GLASSES			
7740 Boro-silicate	B_2O_3, SiO_2	Na_2O, Al_2O_3	600 C
1723 Alumino-silicate	Al_2O_3, MgO, CaO, SiO_2	B_2O_3, BaO	700 C
7930 High Silica	SiO_2	B_2O_3	1150 C
GLASS CERAMICS			
LAS I	$Li_2O, Al_2O_3, MgO, SiO_2$	ZnO, ZrO, BaO	1000 C
LAS II	$Li_2O, Al_2O_3, MgO, SiO_2, Nb_2O_5$	ZnO, ZrO_2, BaO	1100 C
LAS III	$Li_2O, Al_2O_3, MgO, SiO_2, Nb_2O_5$	ZrO_2	1200 C
MAS	MgO, Al_2O_3, SiO_2	BaO	1200 C
BMAS	BaO, MgO, Al_2O_3, SiO_2		1250 C

TABLE - 18
Properties of silicon nitride and carbon/silicon nitride materials (109).

PROPERTY	Si_3N_4	C/Si_3N_4
Bulk density (g/cm^3)	3.44	2.7
Fibre content (vol. %)	-	30
Bending strength (MPa)	473 ± 30	454 ± 42
Young's modulus (GPa)	247 ± 16	188 ± 18
Fracture toughness ($MPa\sqrt{m}$)	3.7 ± 0.7	15.6 ± 1.2
Work of fracture (J/m^2)	19.3 ± 0.2	4770 ± 770

TABLE - 19
Room temperature strengths of RBSN * and SiC/RBSN (122)

TEST	AXIAL STRENGTH (MPa)		
	0% FIBRE	23% FIBRE	40% FIBRE
Four point bend	107 ± 26	539 ± 48	616 ± 36
Three point bend	-	717 ± 80	958 ± 45
Tensile	-	352 ± 73	536 ± 20

* RSBN - Reaction bonded silicon nitride

TABLE - 20
Properties of brittle fibre/SiC matrix composites.

REF	REINFORCEMENT	MATRIX	VOL%	COMP. DENSITY % Th.	4 POINT BENDING STRENGTH *MPa*	K_{1c} $MPa\sqrt{m}$
125	*SiC* Fibres	*SiC*	45	70-77	213-230	-
			39.5	68-75	224-410	-
	SiC cloth	*SiC*	41.6	75-90	419-437	-
			37.9	73-89	187-217	-
	SiC chopped	*SiC*	25.4	51-81	90-177	-
	fibres		21.9	71-77	50-94	-
119	*SiC* cloth	*SiC*	35.5	62-83	72-107	1.8-3.6
	plain weave		46.3	65-85	71-196	-
	satin weave	*SiC*	50.2	68-84	44-97	-
99	*SiC* chopped	*SiC*	16.8	69-82	61-106	-
	fibres		24.3	68-76	74-98	-
			25.4	51-81	90-177	-
	SiC cloth	*SiC*	41-45	64-90	107-476	-
	SiC fibres	*SiC*	39-57	68-77	38-410	-
121	*SiC* fibres	*SiC*	-	>90	320	>25
	C fibres	*SiC*	-	>90	530	>25

TABLE - 21

Room temperature properties of some un-reinforced ceramics and ceramic matrix composites (129).

MATERIAL	FLEXURAL STRENGTH MPa	FRACTURE TOUGHNESS $K_{1c}, MPa\sqrt{m}$
Al_2O_3	550	4-5.0
SiC whiskers/Al_2O_3	800	8.7
SiC	500	4.0
SiC fibres/SiC	750	25.0
ZrO_2	200	5.0
SiC (BN coated fibres) /ZrO_2	450	22.0
Borosilicate glass	60	0.6
SiC fibres/borosilicate glass	830	18.9
Glass ceramic	200	2.0
SiCfibres/glass ceramic	830	17.0
Reaction bonded Si_3N_4	260	2-3.0
SiC whiskers/reaction bonded Si_3N_4	900	20
Hot pressed Si_3N_4	470	3.7-4.5
SiC whiskers/hot pressed Si_3N_4	800	56

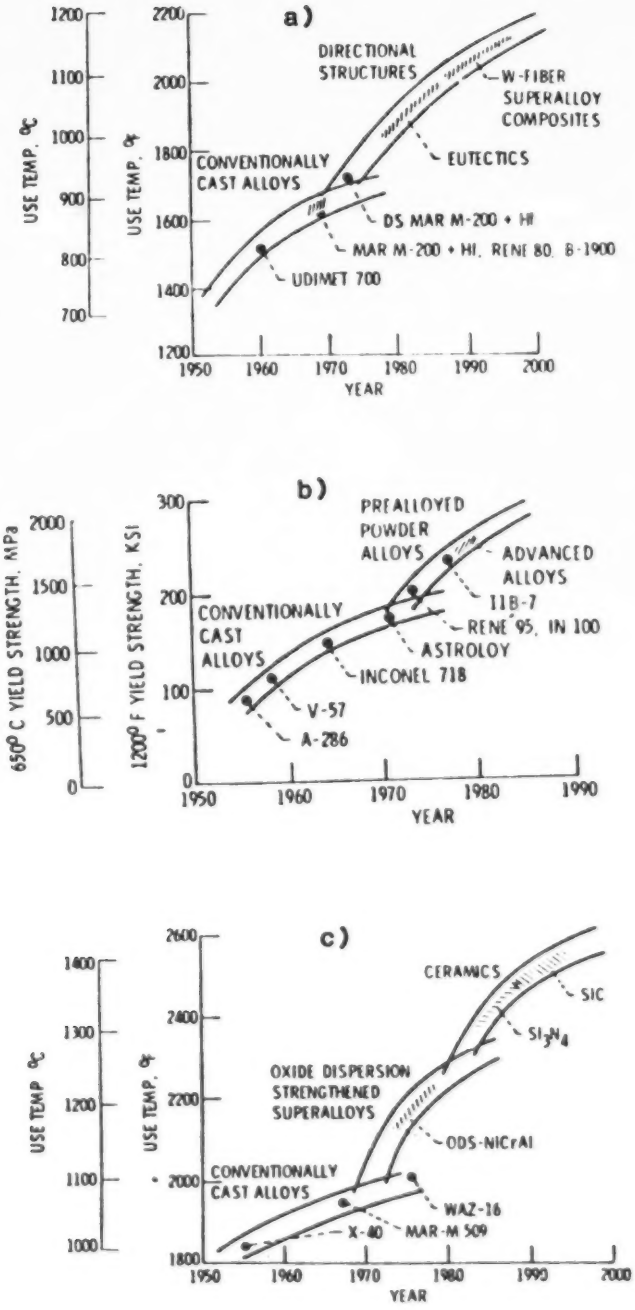

Figure 1: Projected use temperature of : a) turbine blade alloys, b) turbine disc alloys and c) turbine vane materials (3).

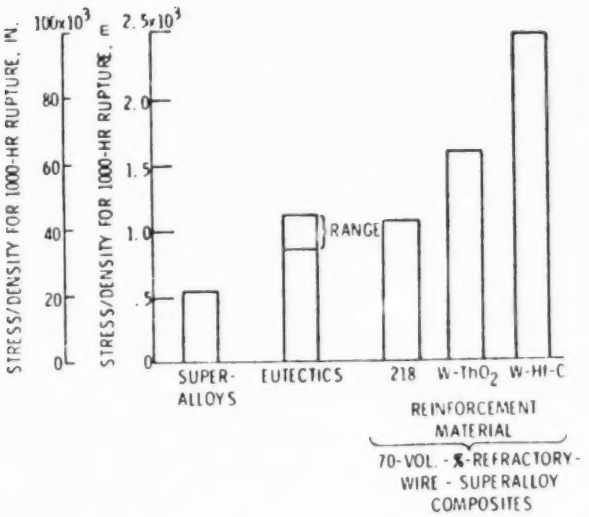

Figure 2: 1000 hours stress rupture properties of refractory wire superalloy composites at 1090 C (12).

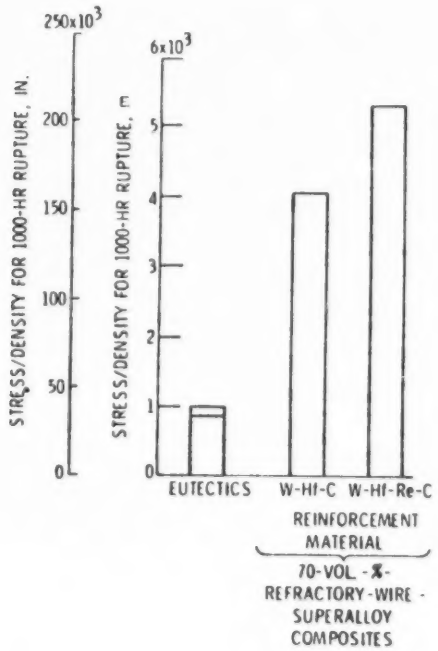

Figure 3: Projected 1000 hours composite rupture properties with diffusion barrier at 1090 C (12).

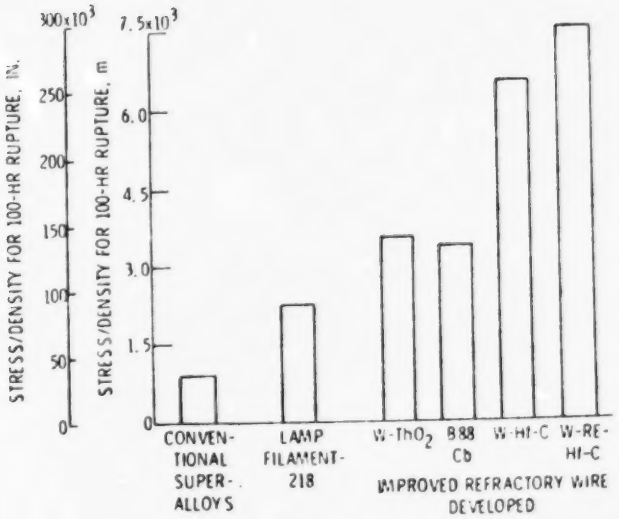

Figure 4: 100 hours stress rupture properties of refractory alloy fibres at 1090 C (12).

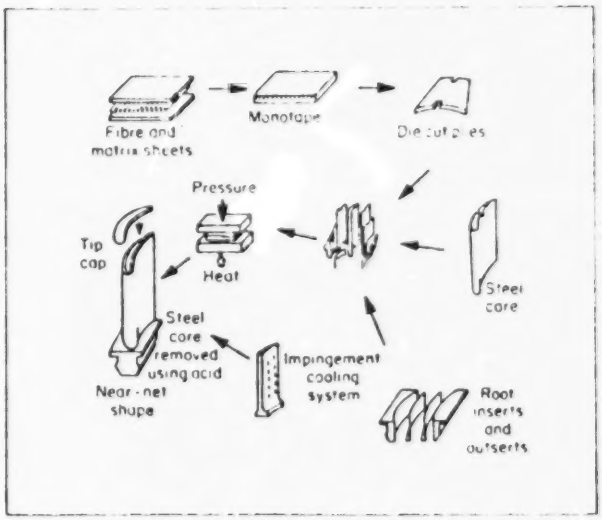

Figure 5: Schematic of TFRS fabrication process.

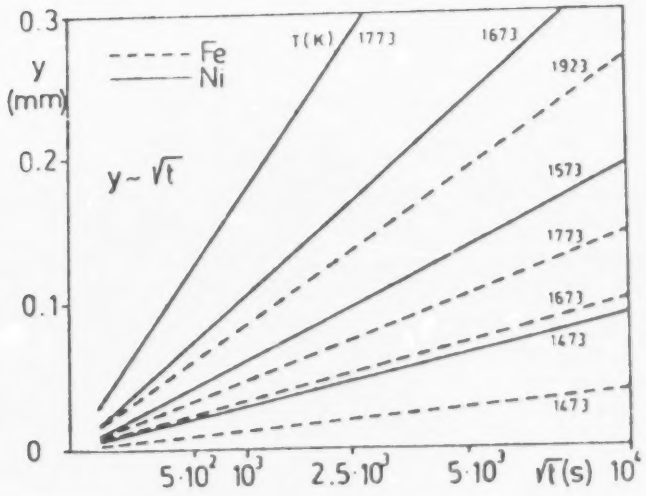

Figure 6: Propagation of the recrystallization front in W wire activated by Ni and Fe in the temperature range 1473–1923 K (117).

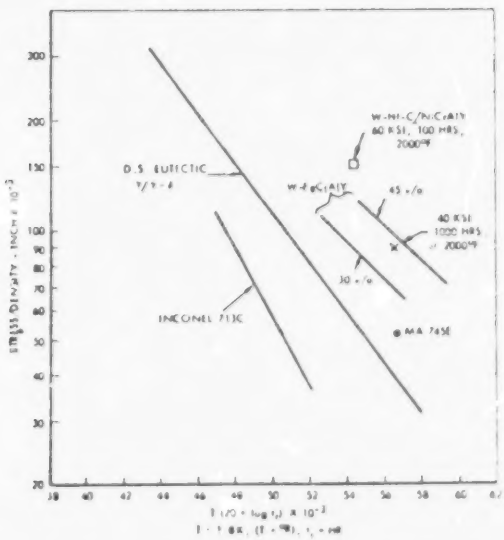

Figure 7: Comparitive density normalized Larson-Miller stress rupture curves (58).

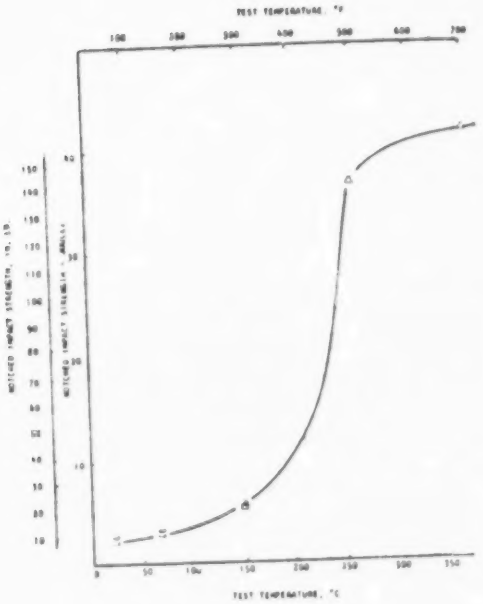

Figure 8: Notched impact strength versus temperature for $W/FeCrAlY$ (58).

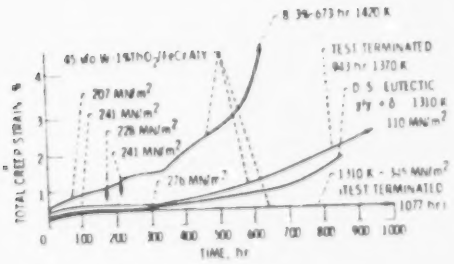

Figure 9: Comparitive data for $W - 1\%ThO_2/FeCrAlY$ and DS eutectics. (57).

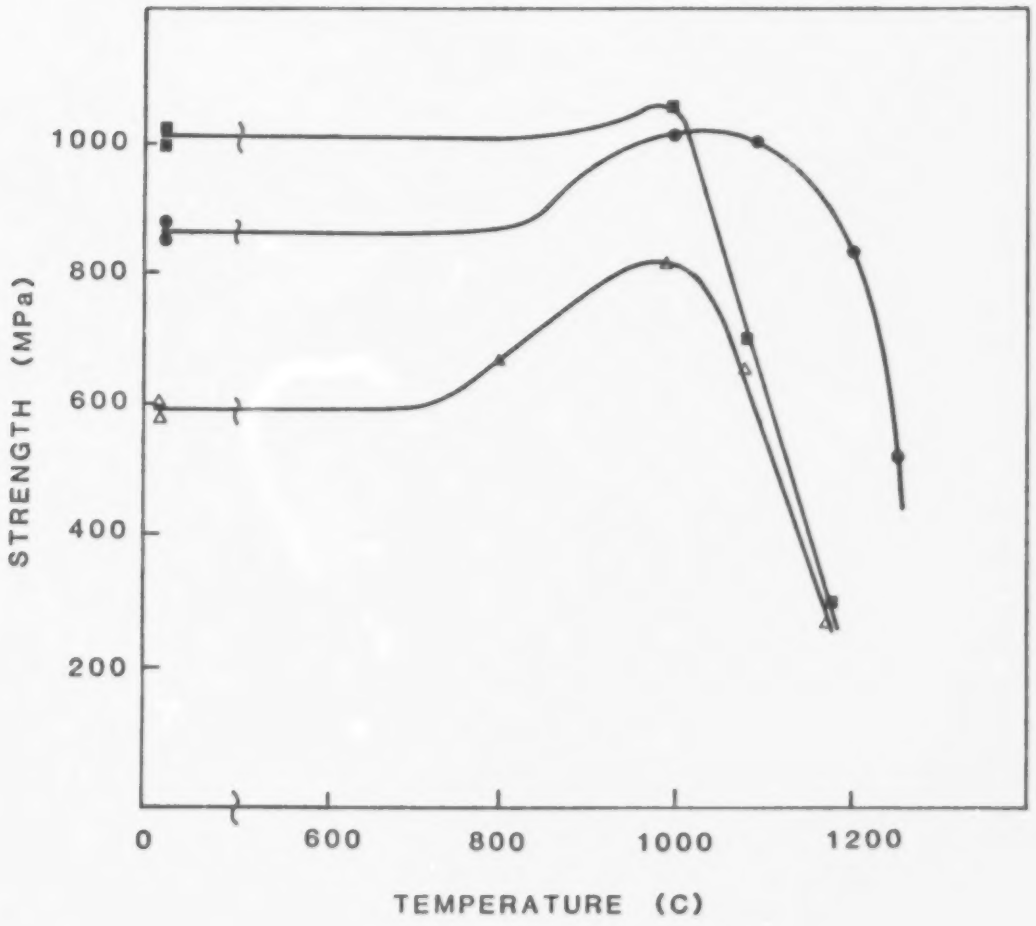

Figure 10: Three point flexural strength in argon versus temperature for unidirectional LAS matrix *SiC* yarn reinforced composites, (△) LAS I matrix, (●) LAS II matrix and (■) LAS III matrix. (126).

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M. U. Islam, W. Wallace and A. Y. Kandeil

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1. High temperature composites
2. Metal matrix composites
3. Ceramic matrix composites

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This paper provides a review of develoments in artificial, metal and ceramic matrix composites with potential for high temperature applications, such as in the hot sections of gas turbine engines. Emphasis is placed on development occuring since 1975. An attempt is made to assess the current level of activity and to identify outstanding problems and research directions for the future. To provide a basis for these discussions, the status prior to 1975 is also briefly reviewed.

ADDRESS/ADRESSE 16

Mr. J. Pleog, Director
Division of Mechanical Engineering
Montreal Road, Ottawa, Ontario
K1A OR6 (613)993-2424

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